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Taste and Odor in Drinking Water: Sources and Mitigation Strategies

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Summary

Taste and odor (T&O) control is an important issue for drinking water suppliers because consumers react very sensitively to changes in the organoleptic quality of their drinking water. As most of the T&O compounds in drinking water are algal metabolites, mainly water utilities which treat surface water are affected by T&O problems. Despite intensive research in this field, it is difficult and time-intensive to assess the involved T&O compounds in the case of consumer complaints. This can be explained by the individual perception of T&O in drinking water and the very low odor thresholds of many T&O compounds (typically in the low ppt-range).

While worldwide many water utilities are confronted with sometimes massive T&O problems, widespread T&O problems have been avoided in Switzerland by the application of a multi-barrier drinking water treatment and water resources protection. However, if parts of the current treatment trains are to be replaced by new treatment techniques in future, e.g., membrane filtration, it has to be guaranteed that T&O problems do not evolve. Therefore, detailed knowledge of the natural occurrence of T&O compounds as well as their behavior during drinking water treatment is needed.

The present study aimed to assess the natural occurrence and seasonal fluctuations of T&O compounds in surface waters. Towards this end, an analytical approach that is widely applied in the food and flavor industry has been further developed to detect and quantify T&O compounds in the low ppt-range in natural and drinking waters. Using this combined instrumental and organoleptic method, the T&O situation in three Swiss lakes (Lake Greifensee, Lake Zurich and Lake Lucerne) was investigated. Furthermore, the method was applied to solve a case of consumer complaints about a musty odor in the tap water.

Another important topic of this study was the investigation of the behavior of selected T&O compounds during drinking water treatment. The main focus was on ozone-based oxidation processes because they have proofed to be very appropriate for T&O control in numerous studies. Bench-scale experiments were performed to determine second order rate constants for the reaction of eleven relevant T&O compounds with ozone and hydroxyl radicals, which are powerful oxidants that are formed during the decomposition of aqueous ozone. These kinetic data provide a useful tool to estimate and consequently, optimize the removal of T&O compounds during ozonation. Additionally, ozonation experiments with natural water were

performed on laboratory- and pilot-scale to evaluate the applicability of ozonation for T&O control in real reactor systems. Apart from the T&O removal, the formation of undesired oxidation by-products was investigated in these experiments.

The applied analytical method, which combined olfactory with GC-MS detection after extraction with headspace-SPME (solid phase micro extraction), proved to be highly sensitive and selective for the analysis of T&O compounds in natural and drinking water. The detection limits for the investigated compounds were in the sub ppt to low ppt-range.

In the course of this study, six T&O compounds could be identified in the three investigated lakes (geosmin, 2-methylisoborneol (MIB), β -ionone, β -cyclocitral, 2-isobutyl-3-methoxypyrazine, 2-isopropyl-3-methoxypyrazine). As reported in previous studies, the identified compounds showed a general correlation to phytoplankton and therefore, higher abundance in eutrophic water bodies (Lake Greifensee > Lake Zurich > Lake Lucerne). But even in eutrophic Lake Greifensee, the peak concentrations of the identified T&O compounds amounted only to a few ng L^{-1} , while the literature contains studies which determined several 100 ng L^{-1} of certain T&O compounds in surface waters. In some cases, though, the low T&O concentrations in this study were still higher than the respective odor threshold concentrations. Furthermore, a substantial part of the identified T&O compounds was not dissolved in the lake water, but particle-bound in the phytoplankton cells. This intracellular fraction was particularly pronounced for β -ionone in Lake Zurich. Our data revealed that the occurrence of β -ionone was largely influenced by the cyanobacterium *Planktothrix rubescens*. This is the first time that a correlation between β -ionone and this species in natural waters has been reported. This is a relevant information for water utilities which treat surface water because *Planktothrix rubescens* can be abundant in surface waters during fall and winter. When this water is treated without a preceding removal of particles, particle-bound compounds such as β -ionone might be released during drinking water treatment and eventually get into the tap water.

The ozonation experiments showed that all investigated compounds were oxidized by 50% or more during ozonation of natural waters under typical drinking water treatment conditions. This was mainly due to the high reactivity of these compounds towards hydroxyl radicals, which are formed during the decomposition of aqueous ozone. However, for a 90% removal of T&O compounds with low reactivity towards ozone, such as geosmin or MIB, high ozone

doses ($> 2 \text{ mg L}^{-1}$) had to be applied. These ozone doses are likely to cause problems with undesired by-products. In this context, the formation of the potentially carcinogenic bromate requires full attention. An accelerated removal of ozone-resistant T&O compounds and a reduced bromate formation could be achieved with an advanced oxidation process (AOP) by adding hydrogen peroxide to the water during ozonation. Laboratory- and pilot-scale experiments showed that the AOP $\text{O}_3/\text{H}_2\text{O}_2$ is a flexible drinking water treatment process which allows a fast adjustment to T&O episodes. Furthermore, existing ozone reactors can easily be upgraded to function as AOPs. But also conventional ozonation in combination with activated carbon filtration is able to almost completely retain dissolved T&O compounds from surface waters

Concluding, the low T&O concentrations in the investigated lakes and the multi-barrier approach that is chosen for surface water treatment in Switzerland, make it unlikely that T&O problems could be generated in the investigated areas from dissolved algal T&O compounds. As for the particle-bound compounds, their potential release during drinking water treatment is strongly dependent on the treatment processes, i.e., on the sequence of removal and oxidation processes. In the investigated lakes, though, the concentrations of particle-bound compounds are probably also too low to generate T&O problems. Nevertheless, future changes (climate, nutrients) might affect the phytoplankton community and accentuate the production of particle-bound T&O compounds.

While worldwide most of the reported T&O problems apart from chlorine residuals in the tap water can be traced back to algal metabolites and could be mitigated by an optimized drinking water treatment and appropriate measures at source level, e.g., limitation of algal growth through a reduction of the nutrient load into surface waters, T&O problems in Switzerland are probably mainly generated in the distribution system. In a case study, the application of the presented method for T&O analysis allowed to identify the potent T&O compound 2,4,6-trichloroanisole (TCA) in the tap water of a Swiss town which was confronted with consumer complaints. Experiments conducted in the laboratory showed that the addition of low chlorine doses as residual disinfectant and biofilms in the distribution system played a key role in the formation of TCA. Based on these results, appropriate counter-measures, such as water distribution without a residual disinfectant, could be taken to mitigate the T&O problem.

Zusammenfassung

Geruchs- und Geschmacksstoffe (kurz: T&O für taste and odor) stellen eine grosse Herausforderung für die Wasserversorger dar, da viele Konsumenten sehr besorgt reagieren, wenn das Trinkwasser nicht geschmacks- und geruchsneutral ist. Betroffen sind vor allem Seewasserwerke, da das Auftreten von vielen T&O-Stoffen eng an das Wachstum von Phytoplankton gekoppelt ist. Trotz intensiver Forschung auf diesem Gebiet ist die Erfassung von T&O-Substanzen in einem Geruchsfall schwierig und zeitaufwendig. Häufig sind diese Stoffe nämlich in sehr geringen Konzentrationen im Wasser vorhanden (ng L^{-1} -Bereich) und haben auch Geruchsschwellen in diesem tiefen Bereich.

Während weltweit gesehen viele Wasserversorgungen mit zum Teil massiven Geruchsproblemen konfrontiert sind, konnten in der Schweiz grossflächige T&O-Probleme bislang durch mehrstufige Verfahren bei der Wasseraufbereitung weitgehend vermieden werden. Durch den vermehrten Einsatz von einfacheren Verfahrensketten (z.B. Membranfiltration), muss jedoch gewährleistet bleiben, dass hierzulande nicht plötzlich vermehrt T&O-Probleme auftreten. Dazu ist nebst dem Wissen über das natürliche Vorkommen von T&O-Stoffen ein tiefes Verständnis der einzelnen Prozesse der Trinkwasseraufbereitung in Bezug auf die Elimination dieser Stoffe notwendig.

Das Ziel der vorliegenden Doktorarbeit war einerseits die Weiterentwicklung und Anwendung einer analytischen Methode, um T&O-Stoffen auf die Spur zu kommen. Mit Hilfe dieser kombinierten olfaktorischen und instrumentalanalytischen Methode wurde die derzeitige T&O-Situation in der Schweiz evaluiert. Dazu wurden Wasserproben von drei Seen mit unterschiedlichem Nährstoffgehalt (Greifensee, Zürichsee und Vierwaldstättersee) auf potentielle T&O-Stoffe hin analysiert. Ausserdem kam die Methode zum Einsatz, um einen Fall zu lösen, bei welchem der Geruchsstoff erst im Leitungsnetz gebildet wurde.

Ein weiterer wichtiger Bestandteil dieser Arbeit bildete die Untersuchung des Verhaltens von T&O-Stoffen während der Trinkwasseraufbereitung. Der Fokus lag hierbei auf ozonbasierten Prozessen, da diese weit verbreitet sind und sich in der Praxis sowie in unzähligen Studien als gut geeignet für die Entfernung von T&O-Stoffen erwiesen haben. In Laborexperimenten wurden Geschwindigkeitskonstanten 2. Ordnung für die Reaktion von elf relevanten T&O-Stoffe mit Ozon und OH-Radikalen ermittelt. Diese kinetischen Daten sind notwendig, um die Oxidation von T&O-Stoffen während der Wasseraufbereitung abschätzen und so den Prozess optimieren zu können. Daneben wurden aber auch Versuche mit natürlichem Wasser

durchgeführt, welche das praktische Potential der Ozonung aufzeigen sollten. In diesen Versuchen, welche sowohl im Labor- als auch im Pilotmassstab durchgeführt wurden, stand neben der Geruchsstoffelimination auch die Bildung unerwünschter Oxidationsnebenprodukte im Zentrum.

Die verwendete analytische Methode erwies sich als sehr geeignet, um auch in komplexen Umweltproben (wie z.B. Algenaufschlüssen) selektiv Geruchsstoffe bis zu einer Konzentration von 1 ng L^{-1} zu detektieren und zu quantifizieren. Die Methode wurde basierend auf SPME (solid phase micro extraction)-GC-MS entwickelt. Neben der klassischen MS-Detektion wurde ein Olfaktometer eingebaut, um eine parallele sensorische Charakterisierung der Probe mit der Nase vornehmen zu können.

Während der Seenstudie im Jahr 2006 konnten so insgesamt sechs verschiedene Geruchsstoffe identifiziert werden (Geosmin, 2-Methylisoborneol, 2-Isopropyl-3-methoxypyrazin, 2-Isobutyl-3-methoxypyrazin, β -Cyclocitral und β -Ionon). Konsistent zur verfügbaren Literatur nahmen die T&O-Konzentrationen tendenziell mit zunehmendem Eutrophierungsgrad zu (Greifensee > Zürichsee > Vierwaldstättersee). Die identifizierten Geruchsstoffe lagen jedoch in vergleichsweise tiefen Konzentrationen von wenigen ng L^{-1} vor (in stark eutrophierten Gewässern sind Einzelstoffkonzentrationen von mehreren 100 ng L^{-1} möglich). Dennoch wurden die Geruchsschwellen für gewisse Verbindungen in den untersuchten Seen überschritten. Auffällig an den erhobenen Daten war zudem, dass ein bedeutender Anteil der Geruchsstoffe nicht im Wasser gelöst, sondern in Algenzellen gebunden vorlag. Dank einer gezielten Messkampagne im Zürichsee im Jahr 2007 konnte zum Beispiel gezeigt werden, dass β -Ionon vor allem in Zellen des Cyanobakteriums *Planktothrix rubescens* gebildet wird. Dies ist für Wasserversorger insofern von Bedeutung, als diese Organismen während der winterlichen Seendurchmischung häufig auf Tiefe der Ansaugstutzen und somit in die Trinkwasseraufbereitung gelangen. Dort können die gebundenen Stoffe unter Umständen freigesetzt werden.

Die Abbauxperimente haben gezeigt, dass während der Ozonung von natürlichem Wasser alle untersuchten Geruchsstoffe oxidiert werden. Dies liegt vor allem daran, dass die Stoffe durch unselektiv reagierende OH-Radikale oxidiert werden, welche beim Ozonzerfall entstehen. Jedoch sind für langsam mit Ozon reagierende Verbindungen (wie Geosmin oder 2-Methylisoborneol) zum Teil sehr hohe Ozondosen ($> 2 \text{ mg L}^{-1}$) nötig, um einen Abbau von über 90% zu erzielen. Bei diesen Ozondosen werden die Wasserversorgungen allerdings

neben hohen Energiekosten auch mit der Bildung unerwünschter Nebenprodukte (allen voran das potentiell krebserregende Bromat) konfrontiert. Ein schnellerer Abbau von ozonresistenten Geruchsstoffen bei gleichzeitig minimierter Bromatbildung lässt sich mit Prozessen der weitergehenden Oxidation erreichen. In Labor- und Pilotversuchen hat sich gezeigt, dass solche Prozesse (z.B. O_3/H_2O_2) wirkungsvolle Instrumente sind, um schnell auf allfällige Geruchsepisoden aus dem Seewasser zu reagieren. Von Vorteil ist ausserdem, dass bestehende Ozonanlagen zu diesem Zweck gezielt aufgerüstet werden können.

Insgesamt kann davon ausgegangen werden, dass gelöste Geruchsstoffe während der konventionellen Seewasseraufbereitung mit Ozon und Aktivkohle nahezu vollständig eliminiert werden. In Kombination mit den bereits tiefen Konzentrationen in den untersuchten Seen ist nicht davon auszugehen, dass in den entsprechenden Regionen Geruchsprobleme im Trinkwasser durch gelöste Stoffe aus dem See auftreten. Im Gegensatz dazu haben partikulär gebundene Stoffe jedoch das Potential, einen Teil der Aufbereitung unbeschadet zu überstehen und somit in möglicherweise wahrnehmbaren Konzentrationen ins Reinwasser zu gelangen. In den untersuchten Seen sind die Konzentrationen der partikulär gebundenen Geruchsstoffe zurzeit jedoch ebenfalls so tief, dass Geruchsprobleme durch eine allfällige Freisetzung dieser Stoffe während der Wasseraufbereitung wenig wahrscheinlich sind. Zukünftige Änderungen der Umweltbedingungen (Klima, Nährstoffe) können aber einen starken Einfluss auf das Phytoplankton und die Produktion von Geruchsstoffen haben. Vor diesem Hintergrund ist es wichtig, die Freisetzung und Entfernung von partikulär gebundenen Stoffen in verschiedenen Trinkwasseraufbereitungsprozessen (Filtrations- und Oxidationsschritte) eingehend zu untersuchen.

Während weltweit gesehen T&O Probleme mehrheitlich aus Oberflächengewässern stammen und mit geeigneten Massnahmen im Gewässerschutz (Limitierung des Algenwachstums durch reduzierte Nährstoffzufuhr) und einer Optimierung der Trinkwasseraufbereitung minimiert werden können, sind die beobachteten Geruchsprobleme in der Schweiz wohl vor allem auf Probleme im Leitungsnetz zurückzuführen. Wenn Trinkwasser lange in Leitungen verweilt, kann es zu Geruchsproblemen kommen, da mikrobiologische Prozesse in Biofilmen in den Leitungen potente Geruchsstoffe hervorrufen können. Mit der oben beschriebenen spurenanalytischen Methode konnte in zwei Haushalten einer von Geruchsproblemen betroffenen Gemeinde der potente Geruchsstoff 2,4,6-Trichloroanisol (moderiger Geruch) nachgewiesen werden. In anschliessenden Laborversuchen konnte die Bildung dieses Stoffes rekonstruiert und gezeigt werden, dass im vorliegenden Fall vor allem das Hinzufügen von

niedrigen Dosen eines chlorhaltigen Netzschutzes nach der Wasseraufbereitung sowie Biofilme im Verteilnetz und in Haushaltsinstallationen zur Bildung dieses Stoffes führten. Aufgrund dieser Ergebnisse konnten konkrete Massnahmen abgeleitet werden (z.B. Verzicht auf chlorhaltigen Netzschutz), mit denen sich die Bildung von Trichloranisol entscheidend beeinflussen liess.

Chapter 1

General Introduction

1.1 Background

Taste and odor (T&O) control has become an important issue for drinking water suppliers worldwide. Today, most of the consumer complaints which are addressed to water utilities are related to bad taste or odor of drinking water [1]. Although aesthetic aspects such as color or T&O are typically non-problematic with regard to health aspects compared to the microbiological quality as well as the presence of micropollutants and heavy metals, consumers react very sensitively to changes in the organoleptic quality of their drinking water. The reason for this is that unlike the microbiological and chemical quality of the water, aesthetic aspects can be assessed directly with human senses. Some potent T&O compounds can be perceived at very low concentrations in the ng L^{-1} -range. These organoleptic effect levels are several orders of magnitudes lower than toxic effect levels of heavy metals or micropollutants. Although these low T&O concentrations do not pose a health risk, many consumers are afraid that the occurrence of T&O compounds in their drinking water is consistent with a decline in the microbiological quality and that therefore, the water is not safe to drink any more [2, 3]. Indeed, as several T&O compounds are produced by cyanobacteria, their occurrence might reveal the presence of cyanotoxines in the water [4]. Still, in most cases this general concern is not justified since no other water quality parameters are affected by T&O.

Nevertheless, the anxiety of the consumers and the consequent lack of trust can cause substantial adverse public impacts such as reduced funding for the maintenance of the infrastructure (mainly distribution system) [1]. Consequently, the water utilities are anxious to avoid or quickly and efficiently mitigate T&O problems. A fast and reliable identification of the involved T&O compounds and their origins is required to meet this task. This is often quite difficult to achieve, though, which in many cases prevents water utilities from applying well-designed counter-measures. The reasons for these difficulties are manifold. On the one hand, the organoleptic perception is very individual both with respect to the description of the flavor as well as to threshold concentrations. This makes it very challenging to evaluate consumer complaints. On the other hand, the detection of T&O compounds is time-consuming and requires sophisticated analytical methods. Non-target analysis of T&O compounds with conventional instrumental methods, i.e., GC-MS in combination with different extraction methods, is often impossible because the low T&O concentrations are masked by the background of the matrix. The alternative sensory analysis by trained specialists provides information on the overall organoleptic perception of a water sample, but

normally does not allow the detection of single T&O compounds. Mixtures of T&O compounds can render a successful detection even more difficult due to synergistic and antagonistic effects [5].

1.2 Origin of drinking water related T&O compounds

As stated above, successful prevention or mitigation of T&O problems is only possible when the involved compounds and their origins are known. The most important T&O compounds reported in literature are chlorine and the earthy-musty compounds geosmin, 2-methylisoborneol (MIB) and 2,4,6-trichloroanisole [6, 7]. Although many other compounds have been identified during T&O events in drinking water (a good overview of T&O compounds is given in ref. [8]) since the “discovery” of earthy geosmin over 40 years ago [9], some fundamental questions related to T&O problems remain unanswered. For example, the origins and factors influencing the production of many T&O compounds are still poorly understood [10].

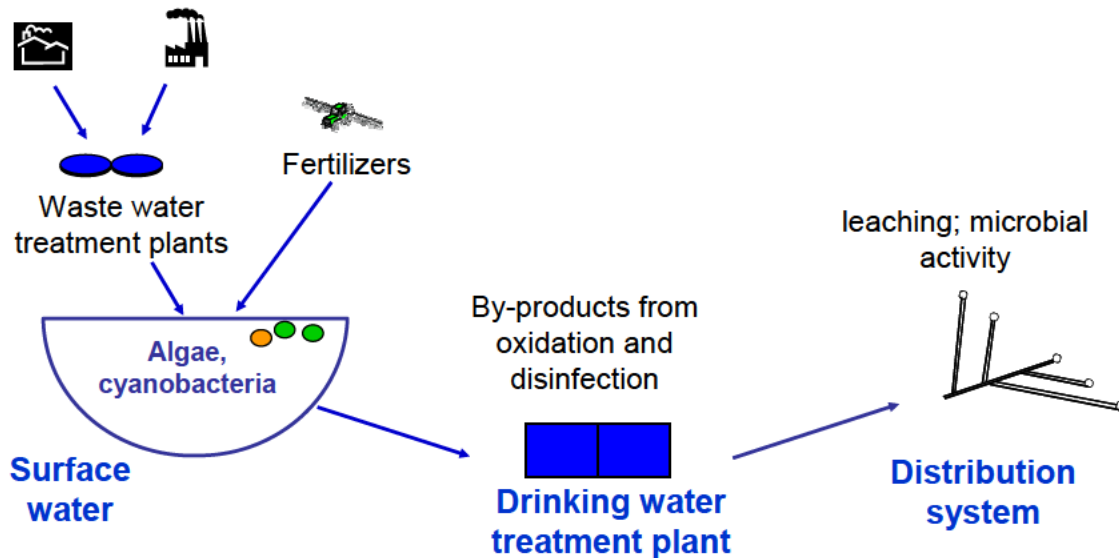


Figure 1-1: Origins of T&O compounds that are relevant for drinking water

According to Figure 1-1, three main origins of T&O problems can be distinguished. Firstly, a large fraction of the T&O compounds that are described in literature is formed in surface waters. These compounds are produced by phytoplankton and often show a strong spatial and seasonal pattern according to the growth of their producers. As the biomass in surface water is strongly related to the nutrient load, municipal and industrial waste water as well as the agricultural practice, e.g., the use of fertilizers and manure application, largely influence the growth of phytoplankton. Typically, the highest T&O concentrations, which can reach several hundred nanograms per liter or even more than 1 µg L, are found in the epilimnion of

eutrophic water bodies during summer. Approximately 200 algal T&O compounds have been identified to date. Table 1-1A gives an overview of the most important surface water related T&O compounds. The physiological role of these compounds is not well understood although some have been described as repellants against grazers or pheromones [10]. While it is probable that some T&O compounds are biologically active, others are formed as metabolic by-products and only released to the water when the cell membrane is damaged. This particle-bound fraction can be a substantial source of T&O problems when it is released from damaged cells of algae and bacteria during drinking water treatment (see below). Depending on the biological activity of phytoplankton, the particle-bound T&O fraction can reach considerably higher concentration levels than the dissolved fraction [11].

Secondly, some potent T&O compounds can be formed as by-products during oxidation and disinfection of drinking water (Table 1-1C). The extent of the formation of these by-products depends strongly on the composition of the water matrix and can be minimized by the use of adequate treatment trains. The use of chlorine, for example, can lead to the formation of bromophenols, such as 2,6-dibromophenol with a low odor threshold of 0.5 ng L^{-1} [12], in the presence of bromide [13] or trihalomethanes such as iodoform in the presence of iodide [14]. Apart from organoleptic aspects, iodinated organic compounds are also problematic with regard to health aspects. Also the use of ozone results in the formation of intermediate reaction products, such as short-chain aldehydes, that could impart odors in drinking water. However, by-products of ozonation have much higher T&O thresholds than by-products of chlorination and are usually easily removed by the subsequent biological activated carbon filtration [15].

Finally, some T&O compounds are generated in the distribution system [16]. Of major importance in this context are compounds that are leaching from polyethylene pipes [17] and other drinking water system components [18] as well as compounds that are formed during microbiological processes in biofilms [19]. The most potent T&O compound in this context is 2,4,6-trichloroanisole with a reported odor threshold of 30 pg L^{-1} [20]. Distribution generated T&O problems are a major concern to water suppliers because there is no barrier available to remove these compounds before they reach the tap. Therefore, special attention has to be paid on the choice of appropriate components and the maintenance of distribution systems. Some of these distribution system related T&O problems can be avoided or masked by the use of a residual disinfectant (chlorination). However, the choice of chlorination versus non-chlorination is a trade-off between positive secondary effects and the chlorine odor in the tap water, which is likely to cause consumer complaints.

Table 1-1 gives an overview of the most relevant T&O compounds in drinking water. Table 1-1 is restricted to compounds with very low odor thresholds and/or compounds that have been reported to cause T&O problems in drinking water. For a broader overview of potential T&O compounds in drinking water, the reader is referred to refs [8, 10, 18].

Table 1-1. Relevant T&O compounds in drinking water

A) Natural T&O compounds in surface waters

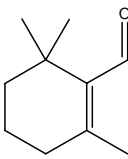
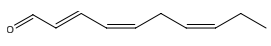
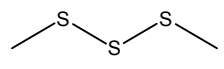
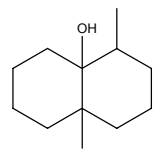
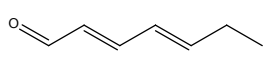
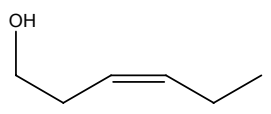
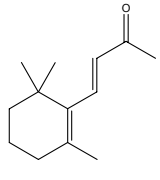
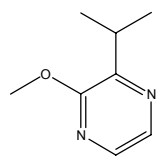
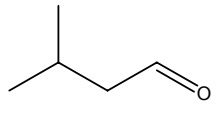
compound	structure	odor	odor threshold (ng L ⁻¹)	source
β -cyclocitral		fruity	19'000 [21]	cyanobacteria
2-trans,4-cis,7-cis-decatrienal		fishy	20'000 [10]	green algae
dimethyl trisulfide		decaying vegetation	10 [21]	bacterial decomposition of algal blooms and grass
geosmin		earthy	4 [22]	cyanobacteria and actinomycetes
trans,trans-2,4-heptadienal		fishy	5'000 [8]	green algae
cis-3-hexen-1-ol		grassy	70'000 [21]	green algae
β -ionone		violets	7 [21]	green algae, cyanobacteria
2-isopropyl-3-methoxypyrazine		decaying vegetation	0.2 [22]	Actinomycetes; biochemical decay of grass
3-methyl-1-butanol (isovaleraldehyde)		fusel oil	150 [16]	cyanobacteria

Table 1-1. continued

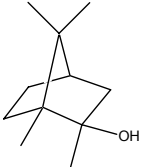
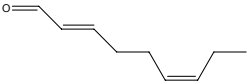
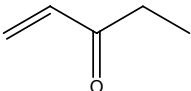
compound	structure	odor	odor threshold (ng L ⁻¹)	source
2-methylisoborneol (MIB)		musty	15 [22]	cyanobacteria and actinomycetes
trans,cis-2,6- nonadienal		cucumber	20 [23]	green algae
1-penten-3-one		fishy - rancid	1250 [21]	green algae, cyanobacteria

Table 1-1. Relevant T&O compounds in drinking water**B) T&O compounds generated in the distribution system**

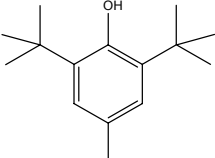
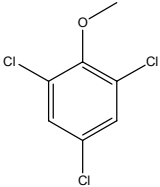
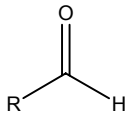
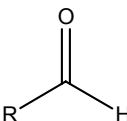
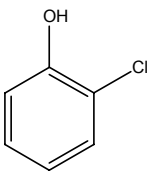
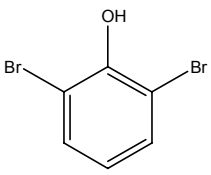
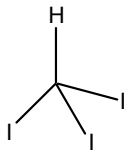
compound	structure	odor	odor threshold (ng L ⁻¹)	source
2,6-di- <i>tert</i> -butyl-4- methylphenol (BHT)		plastic	not available	leaching from polyethylene pipes
2,4,6-trichloroanisole (TCA)		musty	0.03 [20]	methylation of 2,4,6- trichlorophenols by biofilms

Table 1-1. Relevant T&O compounds in drinking water**C) T&O compounds generated during drinking water treatment**

compound	structure	odor	odor threshold (ng L ⁻¹)	source
low molecular weight aldehydes (> heptanal)		fruity	> 30 (undecanal) [16]	ozonation
low molecular weight aldehydes (< heptanal)		very individual (swampy - swimming pool)	200 (heptanal) - 12'000 (propanal) [16]	ozonation
2-chlorophenol		medicinal	360 [22]	chlorination of phenols
2,6-dibromophenol		medicinal	0.5 [12]	chlorination of phenols in the presence of bromide
free chlorine	HO—Cl	chlorinous	25'000 [16]	disinfection with chlorine
iodoform		medicinal	30 [16]	chlorination in the presence of iodide
monochloramine	H ₂ N—Cl	chlorinous	280'000 [16]	disinfection with chloramine

1.3 Drinking water treatment

As depicted above, many T&O compounds are formed in surface waters. These water bodies are important resources for drinking water in densely populated areas. In contrast to groundwater or spring water, the drinking water treatment of surface waters normally requires a multi-barrier approach to fulfill the criteria with respect to disinfection, the removal of particles and toxic compounds as well as to the aesthetic quality. As introduced above, an effective removal of T&O compounds is a key requirement of drinking water treatment. Despite this obvious importance, the knowledge of the behavior of T&O compounds in standard drinking water treatment processes is limited. Generally, a combination of chemical oxidation and adsorptive filtration steps, e.g., ozone/activated carbon, has proved to be most effective in T&O control [24, 25]. However, the literature contains mainly empirical studies with case-specific results, which makes it difficult to make general recommendations for the design of an optimal drinking water treatment train. Kinetic data, especially accurate second order rate constants of oxidation processes, would provide a useful tool to enhance the treatment efficiency.

The following sections provide a short overview of the applicability of oxidation and concentration processes for T&O control in drinking water treatment. In addition, the influence of oxidation on the release of particle-bound T&O compounds is presented. As mentioned above, this release of particle-bound T&O compounds during oxidation processes can become an important source of T&O problems similar to the release of intracellular compounds such as assimilable organic carbon and cyanotoxines [26, 27]. Therefore, typically a removal of intact cells is critical prior to oxidation processes.

Oxidation processes

Ozone and hydroxyl radicals. Although ozone is a selective oxidant that mainly reacts with deprotonated amines, olefins and activated aromatic compounds [28], ozonation has been shown to be a very efficient process for T&O removal [15]. This is mainly due to the fact that two reactive species are involved in this process: ozone and hydroxyl radicals ($\cdot\text{OH}$), which are formed during ozone decomposition. Due to their low selectivity, $\cdot\text{OH}$ are capable to oxidize compounds which show no reactivity toward ozone (such as geosmin, MIB, halogenated phenols and anisoles). Therefore, a high removal efficiency can be expected for these compounds not only in ozonation, but also in advanced oxidation processes (AOPs)

with $\cdot\text{OH}$ as the main oxidant, such as combinations of ozone with H_2O_2 , UV with ozone or UV with H_2O_2 [28, 29].

A recent study conducted with 2-methyl-isoborneol (MIB) producing algae showed that an ozone exposure of roughly $1 \text{ mg L}^{-1} \cdot \text{min}$ destroyed the algal cells quickly and that after only ten minutes, both the dissolved and particulate MIB were completely oxidized [30]. This is a result of the combined action of ozone and $\cdot\text{OH}$.

Chlorine and chlorine dioxide. Chlorine and chlorine dioxide are very selective oxidants which mainly react with activated aromatic systems and deprotonated amines [31]. While the reactivity of chlorine is one to two orders of magnitude lower than the reactivity of chlorine dioxide, the reactivity of these two oxidants with organic compounds is generally much lower than the respective reactivity with ozone (Table 1-2 and refs. [32, 33]). Even at dosages of 10 mg L^{-1} chlorine or chlorine dioxide and contact times of several hours, the T&O residual is usually higher than 50% [30, 34, 35]. However, if the chlorine residuals are high enough, it is likely that they mask the perception of T&O compounds.

Apart from the potential formation of halogenated compounds during chlorination (see above), chlorine and chlorine dioxide were shown to damage the algal cells and release intracellular T&O compounds [30]. Chlorination of natural water with high biomass could therefore lead to an increase in the concentration of dissolved T&O compounds.

Permanganate. Permanganate (mainly applied as potassium permanganate, KMnO_4) reacts predominantly with olefines and phenols. In the case of double bonds, MnO_4^- reacts about 100 times slower than ozone [36]. The reactivity of MnO_4^- toward compounds exhibiting other functional groups, such as MIB and geosmin, is similar to the reactivity of chlorine dioxide [30, 35]. For these slow reacting compounds the adsorption to MnO_2 , which is formed during KMnO_4 oxidation reactions, might be a more important removal mechanism than the oxidation [34].

Experiments conducted with algae showed similar results as were already observed for chlorine: permanganate can damage the algal cells, which can lead to a release of intracellular compounds. Because the reactivity with the dissolved T&O compounds is usually too low for a significant removal, this may lead to an increase in the concentration of dissolved T&O compounds [30, 34].

Kinetics of oxidation processes

The degradation of compounds during oxidation is generally expressed according to eq 1 or the integrated form of eq 2. In eq 1 and eq 2, $k_{P,Ox}$ represents the second order rate constant (in the dimension $M^{-1}s^{-1}$) for the reaction between a compound P and the oxidant (Ox).

$$\frac{d[P]}{dt} = -k_{P,Ox} \cdot [P] \cdot [Ox] \quad (1)$$

$$\ln\left(\frac{[P]}{[P]_0}\right) = -k_{P,Ox} \int [Ox] dt \quad (2)$$

Table 1-2. Second order rate constants for the reaction of selected T&O compounds with various oxidants ($M^{-1}s^{-1}$)

compound	ozone ^a	$\cdot OH$ ^a	ClO_2 ^b	$KMnO_4$ ^c
β -cyclocitral	4'000	7.4×10^9	< 0.01	> 100
geosmin	0.1	7.8×10^9	< 1	< 0.01
cis-3-hexen-1-ol	5.4×10^5	7.5×10^9	< 0.01	> 100
β -ionone	1.6×10^5	7.8×10^9	< 0.01	> 100
2-isopropyl-3-methoxypyrazine	50	4.9×10^9	< 10	< 1
2-methylisoborneol (MIB)	0.4	5.1×10^9	< 1	< 0.01
trans,cis-2,6-nonadienal	8.7×10^5	9.7×10^9	< 0.01	> 100
1-penten-3-one	5.9×10^4	4.7×10^9	< 10^{-4}	> 100
2,6-di- <i>tert</i> -butyl-4-methylphenol (BHT)	7.4×10^4	3.2×10^9	$\sim 10^3$ 000	~ 100
2,4,6-trichloroanisole (TCA)	0.06	5.1×10^9	< 10^{-3}	< 1

^a this study [37]; ^b estimated from [38], rate constants with chlorine are generally about 10 - 100 times lower; ^c estimated from [36]

Table 1-2 provides estimates and own data of these rate constants for the reactions of some of the most relevant T&O compounds (Table 1-1) with different oxidants used in drinking water treatment. Table 1-2 underlines the higher reactivity of ozone to the presented T&O compounds compared to the reactivity of chlorine, chlorine dioxide and permanganate. As for $\cdot\text{OH}$, the differences in the reactivity between the presented T&O compounds are very small because $\cdot\text{OH}$ typically react at nearly diffusion-controlled rates with organic compounds. The second order rate constants for the reactions with ozone and $\cdot\text{OH}$ are discussed in detail in Chapters 4 and 5. Apart from these second order reaction rate constants, the oxidant exposure (concentration integrated over time) governs the degradation of compounds (eq 2). Hence, despite the higher rate constants of ozone and $\cdot\text{OH}$, the overall oxidation effect of other oxidants which exhibit a longer lifetime might still be comparable.

Removal processes

Activated carbon filtration. Activated carbon is either applied in its powdered form (PAC) or as granular activated carbon (GAC) in a deep bed filtration. While the former application can be suitable to react on short-term fluctuations in the organoleptic quality, it is often too expensive to treat the water with PAC on the long run. As for a GAC-filter, its adsorption capacity can be exhausted after a few months due to the loading with natural organic matter. However, even filters which had been in use for several years can still exhibit high T&O removal capacity. One reason for this is the biological activity of the filters. It has been shown that biofilms on the GAC, i.e., biologically active GAC (BAC), can efficiently remove T&O compounds when the bacteria are used to the presence of these compounds [39]. Furthermore, it can be expected that T&O compounds generally exhibit a relatively high affinity towards activated carbon and that they are therefore more easily removed than other more hydrophilic trace contaminants. Indeed, own experiments conducted with different filters revealed that even filters with complete saturation of adsorption sites with natural organic matter can effectively adsorb T&O compounds. These experiments were conducted with β -ionone, 2-isopropyl-3-methoxypyrazine and MIB. Briefly, the experiments revealed a high T&O removal efficiency of GAC-filtration. Deep bed filtration experiments in pilot-scale showed that a bed layer of 1 m was enough to completely retain the investigated compounds even in the case of saturated adsorption sites with natural organic matter. Still, fresh GAC exhibited higher and faster T&O removal capacities. As these experiments were only a small part within an broad GAC study that was performed by several persons, their outcome is not presented in this study but is in preparation for a joint publication [40].

Membrane filtration. Recently, membranes have been implemented in an increasing number of water utilities. The efficiency of membrane processes for T&O removal depends largely on the pore size. A recent study showed that membranes such as nanofiltration (molecular weight cutoff of 200 daltons) and reverse-osmosis (with cutoffs smaller than 200 daltons) can retain T&O compounds to more than 70%, though not completely [41]. In contrast, ultrafiltration with cutoffs of approximately 100'000 daltons is not expected to retain T&O compounds, which usually are small compounds of 100 - 400 daltons. However, ultrafiltration can be combined with powdered activated carbon (CRISTAL®-process), which is very effective for T&O control [41].

1.4 Scope of this study

This project was designed to identify the most relevant T&O compounds in surface waters in Switzerland and to investigate the removal of these compounds during drinking water treatment. This study is structured in four main parts, namely analytical methods, T&O compounds in surface waters, T&O removal during drinking water treatment and T&O problems generated in distribution systems and households.

Analytical method

Chapter 2 describes the analytical method that was developed for the detection of T&O compounds in natural water samples. The presented method is based on head-space solid phase micro extraction (SPME), followed by GC-MS and a parallel detection at an olfactory port. This sensitive method allows to detect and quantify the selected T&O compounds in the low ppt-range even in complex matrices such as phytoplankton suspensions.

T&O compounds in surface waters

Chapter 3 presents detailed results from a field study. This part includes the occurrence of dissolved and particle-bound T&O compounds in the three Swiss lakes Lake Zurich, Lake Greifensee and Lake Lucerne, and elaborates on the temporal and spatial heterogeneity of the identified compounds. The chapter relates the six identified T&O compounds (geosmin, 2-methylisoborneol, β -ionone, β -cyclocitral, 2-isobutyl-3-methoxypyrazine and 2-isopropyl-3-methoxypyrazine) to phytoplankton species that are likely to produce the T&O compounds in the investigated lakes. Additionally, the relevance of the identified compounds for water utilities is discussed.

T&O removal during drinking water treatment

Chapters 4 and 5 present studies which have been performed to investigate the behavior of relevant T&O compounds during drinking water treatment. Relevant in this context means that these compounds were either found in the field study or selected after an extensive literature review. The focus of this part lies on the kinetic description of ozone-based oxidation processes as they are judged to be most effective in T&O control. Towards this end, second order rate constants of the selected T&O compounds with ozone and hydroxyl radicals were determined. Additionally, the applicability of ozonation and ozone-based advanced oxidation processes (AOPs) to mitigate T&O problems in drinking water was investigated in

laboratory- and in pilot-scale experiments. In this context, not only the removal of T&O compounds, but also the formation of the potentially carcinogenic bromate, which is a by-product of the ozonation of bromide-containing waters, was investigated.

T&O problems generated in distribution systems and households

Chapter 6 presents a successful application of the T&O method to resolve a case of consumer complaints in a Swiss town. The chapter includes the identification of the responsible T&O compound, 2,4,6-trichloroanisole (TCA), which was found in the households at concentrations of up to 24 ng L⁻¹. Based on these results, this part elaborates on additional experiments that were performed to investigate the role of biofilms and precursors in the role of TCA-formation and illustrates the effects of mitigation strategies.

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Chapter 2

Analytical method

Application of a Combined Instrumental and Sensory Method to
Detect and Quantify Taste and Odor Compounds in Natural and
Drinking Waters

Abstract

A combined instrumental and sensory method has been developed for the detection of taste and odor compounds at low concentrations in natural and drinking waters. The presented method is based on head-space solid phase micro extraction (SPME), followed by GC-MS and a parallel detection at an olfactory port. The method proofed to be very sensitive and robust with detection limits in the sub ppt to low ppt-range for compounds such as geosmin (detection limit: 1 ng L⁻¹), 2-methylisoborneol (0.5 ng L⁻¹), 2-isopropyl-3-methoxypyrazine (0.5 ng L⁻¹), nonadienal (10 ng L⁻¹), β -cyclocitral (1 ng L⁻¹), β -ionone (1 ng L⁻¹), 2,4,6-tribromoanisole (5 ng L⁻¹) and 2,4,6-trichloroanisole (2 ng L⁻¹).

In three Swiss lake waters (Lake Lucerne, Lake Zurich and Lake Greifensee), the five taste and odor compounds β -cyclocitral, geosmin, β -ionone, 2-isopropyl-3-methoxypyrazine and 2-methylisoborneol could be identified and be reliably quantified in the concentration range of 1 to 20 ng L⁻¹. Furthermore, the method allowed to identify 2,4,6-trichloroanisole (TCA) in a Swiss drinking water, where consumers complained about a musty odor. The absence of this compound in lake water showed that it was formed in the distribution system. TCA in tap water reached concentrations of up to 24 ng L⁻¹.

2.1 Introduction

Worldwide many water utilities are confronted with taste and odor (T&O) complaints. The resulting negative perception of the drinking water quality by the public can lead to a lack of trust in the water industry. Therefore, the water utilities are anxious to quickly and efficiently mitigate T&O problems. Most of the T&O problems reported in literature are characterized as earthy-musty and chlorinous. The most important compounds in this context are geosmin, 2-methylisoborneol, 2,4,6-trichloroanisole and chlorine [1, 2]. However, many other compounds such as unsaturated aldehydes, sulfides, methoxypyrazines and others can provoke T&O problems in drinking water [3]. T&O compounds are usually present in the water at very low concentrations (ppt-level). Hence, fast and sensitive analytical methods are needed to track the responsible compounds and their origin in case of T&O complaints. However, it is often not possible to identify the involved T&O compounds with standard analytical methods, which makes it almost impossible to resolve these problems.

Several methods have been applied successfully to detect selected T&O compounds in the low ng L^{-1} range or at even lower concentrations. These methods are based on extraction techniques such as closed loop stripping analysis (CLSA), solid phase micro extraction (SPME) or stirred bar sorptive extraction (SBSE) combined with GC-MS detection. A short overview of these methods is given in ref. [4]. These methods are appropriate for targeted analysis, i.e., to analyze water for specific T&O compounds. However, in cases where a T&O episode can not be associated to a certain and already known compound, it is helpful to screen water samples for many compounds with organoleptic properties. In this context, the use of the above mentioned GC-MS methods is often limited. The main reason for this limitation is that it is nearly impossible to find T&O compounds amongst all the other compounds which are typically present at much higher concentrations in the water and show up in the chromatograms.

A different approach, which is often chosen by drinking water utilities, is the application of sensory analysis [5]. This approach requires trained specialists, who provide information on the overall organoleptic perception of a water sample. With this approach, it is difficult to detect single T&O compounds and to quantify their concentrations. Furthermore, this method can not be automated, which means that it is rather intensive in terms of labor and time.

A possible solution to these short-comings is the application of a method which combines instrumental trace analysis with the sensory detection of taste and odor compounds. This approach has already found wide application in the food and flavor industry [6-8], where concentrations of flavor compounds are usually much higher than in drinking water. For this purpose, GC-olfactometry (a review on GC-olfactometry was published recently in ref. [9]) coupled to a physical GC detector such as FID or MS is normally used. Descriptions of this combined approach for T&O analysis in drinking waters can be found in the literature [4, 10-13]. Young et al. [10] installed two columns in a GC and connected one column to a MS for quantitative analysis and used the other column as sensory GC for the qualitative detection. With this setting, Young et al. developed a standard method based on the CLSA extraction technique for the targeted analysis of 22 T&O compounds. Yet, a simultaneous detection at the MS and at the olfactory detector port was not possible, but a sample had to be injected twice to gain chemical as well as organoleptic information. Benanou et al. [4] successfully applied a combined SBSE-GC-MS/olfactometry-method for the non-targeted analysis of drinking waters with bad odors. The GC separation was designed in a way that it allowed a simultaneous detection of off-flavors at the olfactory detector port and the MS.

When the two methods described above were published, CLSA and SBSE, respectively, were the best choice for sensitive T&O-analysis with significantly lower detection limits than SPME applications. Recently, however, SPME has re-gained attention as extraction technique because the fiber material has been improved and a whole variety of different fibers with varying properties is now available. Detection limits of sub-ppt levels of the most important T&O compounds and good linearity and precision have been reported recently with headspace SPME-GC-MS [14, 15]. SPME offers the advantage over other extraction techniques that it can be fully automated with a sample throughput of 30 to 50 samples per day (compared to 20 samples per day with SBSE [4]) and that it is completely solvent-free. Additionally, it can be applied as headspace technique with a high selectivity toward volatile compounds. This is an advantage for the analysis of natural waters, which usually exhibit high concentrations of dissolved organic matter. This organic matrix often impairs the analytical sensitivity of methods that extract the volatile compounds directly from the liquid phase.

The present study was conducted to test the applicability of a method based on headspace-SPME-GC-MS combined with an olfactory detector port for the analysis of T&O compounds in natural and drinking waters. Towards this end, the method was validated by determining standard method parameters. Additionally, the suitability of the presented method for the

analysis of real water samples was tested in two applications. On the one hand, the method was used to detect and quantify T&O compounds in several lake water samples. This screening did not only include dissolved T&O compounds but also the particle-bound fraction, which is important to be considered in the context of preventing potential T&O problems in drinking waters. On the other hand, the presented method was applied for the case of a Swiss town with consumer complaints about a musty taste of the local drinking water. The presented method allowed us to identify and quantify the compound which was responsible for the bad taste and to design countermeasures.

2.2 Materials and Methods

2.2.1 Standards and reagents

Geosmin and 2-methylisoborneol were purchased from Wako Chemicals (Osaka, Japan); all the other T&O compounds (Table 2-1) were obtained from Sigma-Aldrich (Buchs, Switzerland) in the highest purity available. All chemicals used for solutions were reagent grade and were used without further purification.

2.2.2 Sampling and sample preparation

Tap water samples were stored in glass bottles at 4°C without specific pre-treatment. Natural water samples (1 L) were taken from each the epilimnion, the metalimnion and the hypolimnion at fixed depths (Table 2-2). The samples were filtered immediately upon arrival (0.45 µm cellulose nitrate filters, Whatman Schleicher & Schuell, Germany) and divided into a dissolved and a particle-bound fraction. The filtrate with the dissolved fraction was transferred to 100 mL glass bottles. The filter residue with the particle-bound fraction was re-suspended in 1 mL nanopure water and transferred to a 1.5 mL micro tube (Sarstedt, Germany), to which approximately 200 µL glass beads (0.11 µm, B.Braun Biotech International, Germany) were added. Bead beating [16] with a cell disrupter (FastPrep FP120, Savant Instruments, Holbrook (NY), USA) was applied to break the cells of algae and bacteria. This procedure was run during 6 × 45 seconds with intermittent cooling of the samples on ice to avoid thermal decomposition of the T&O compounds. A microscopical check of a test sample proved that the cells were destroyed after this preparation step. After sample preparation, all the samples were stored in the dark at 4°C.

For the analysis of the dissolved fraction, 6 mL of the filtered samples were transferred into 10 mL head space vials sealed with silicone-PTFE-septa (BGB Analytics, Switzerland). For the analysis of the particle-bound fraction of the lake samples, 200 µL of the re-suspended residue were added to 5.8 mL MilliQ-water. This dilution and the enrichment of the particles during filtration (the residue of 1 L re-suspended in 1 mL) had to be taken into account to calculate the concentration of the particle-bound T&O compounds in the lake water. Sodium chloride (1.2 g) was added to all samples to enhance the transfer of the compounds into the gas phase. 2-isobutyl-3-methoxypyrazine (IBMP) was used as internal standard for the quantitative analysis and added at a concentration of 10 ng L⁻¹.

2.2.3 Analysis

The analytical method combined classical GC-MS detection with a simultaneous detection at an olfactory detector port (ODP).

Extraction and GC-separation

SPME was used to extract the T&O compounds. SPME was carried out using 1 cm long DVB-Carboxen-PDMS fibers (Supelco, Bellfonte (PA), USA) 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 fiber 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), USA) using a SLB-5MS column (30×0.25×0.25; Supelco, Bellfonte (PA), USA) and helium as carrier gas. The GC was programmed from 50°C (constant temperature for 2 minutes) to 150°C (10°/min) and finally to 220°C (5°/min). The head pressure was held constant at 128 kPa. The length of the transfer columns to both the MS as well as to the ODP have to be carefully adjusted to guarantee the desired split of the helium flow. For this study, a split ratio of 1:1 was chosen, which was achieved by a 60 cm × 0.1 mm ID transfer column to the MS and a 92 cm × 0.15 mm ID transfer column to the ODP. The temperature of the transfer line to the ODP was maintained at 220°C to prevent the compounds from re-condensation.

GC-separation of one sample and SPME-extraction of another sample were performed simultaneously when more than one sample were to be analyzed. With this procedure, the run time for one sample could be shortened substantially from over one hour to 40 minutes.

Detection (T&O screening) and quantification

For the qualitative analysis, an ion trap MS (GCQ, Thermo, Austin (TX), USA) was run in the scan-mode. The ion trap offers the advantage over a quadrupole MS that more structural information on an unknown compound can be gained by applying further fractionation (MSⁿ). Yet, this only works when the MS-signal of the compound can clearly be distinguished from the background noise. Parallel to the MS detection, the compounds were detected at an olfactory detector port (ODP2, Gerstel, Germany). The ODP-signals were triggered with an intensity device (Gerstel, Germany) and recorded in a second chromatogram. As olfactory T&O detection is very individual, the presented method should be carried out by more than

one person and, if possible, trained specialists should assist for this difficult task to ensure a reliable description and detection of odors.

TABLE 2-1. T&O compounds used for targeted GC-MS-analysis

compound (CAS number)	odor	odor threshold (ng L ⁻¹)	source	retention time (min)	masses used for MS detection ^a	detection limits (ng L ⁻¹) ^d
2-isopropyl-3-methoxypyrazine (IPMP) (25773-40-4)	decaying vegetation	0.2 ^e	actinomycetes	10.0	137 , 124	0.5
trans,cis-2,6-nonadienal (557-48-2)	cucumber	20 ^f	algae	11.1	70 , 94	10
2-isobutyl-3-methoxypyrazine (IBMP) ^b (24683-00-9)	vegetable	1 ^e	algae	11.4	124 , 151	n.d. ^c
2-methylisoborneol (MIB) (2371-42-8)	musty	15 ^e	cyanobacteria, actinomycetes	11.9	95 , 107	0.5
β-cyclocitral (432-25-7)	fruity	19000 ^g	cyanobacteria	12.3	152 , 137	1
2,4,6-trichloroanisole (TCA) (87-40-1)	musty	0.03 ^h	bio-methylation of chlorophenols	14.2	210 , 195	2
geosmin (16423-19-1)	earthy	4 ^e	cyanobacteria, actinomycetes	15.8	112 , 126	1
β-ionone (79-77-6)	violets	7 ^g	algae and cyanobacteria	16.8	177 , 41	1
2,4,6-tribromoanisole (TBA) (607-99-8)	earthy- musty	0.03 ^h	bio-methylation of bromophenols	19.7	344 , 329	5

^a bold: quantifier ions; normal font: qualifier ions

^b internal standard for quantitative analysis

^c not determined

^d MS detection; the quantification limit is approximately three times higher than the detection limit

^e [17]; ^f [18]; ^g [19]; ^h [20]

After screening of a sample for off-flavours and identification of T&O compounds at the ODP and the MS, the sample was injected again for quantitative analysis with the MS in the single ion mode (SIM). For practical reasons, it might be appropriate to directly run the MS in the SIM-mode and only analyzing the masses of the most relevant T&O compounds. These compounds are listed in Table 2-1 together with GC-MS parameters needed for their analysis. In this targeted approach, the ODP detection would provide the confirmation that the MS-signal corresponds to the suspected T&O compound. Additionally, it would still give the necessary information if further T&O compounds were present in the sample. To save time for the analysis of a large number of samples it might also be useful to merge some samples and to first screen these composite samples for T&O compounds. For quantitative information, individual samples can be analyzed afterwards if necessary. However, it should be noted that with this procedure the dilution effect might make the detection of T&O compounds impossible if they are present at very low concentrations.

2.2.4 Method validation

The relevant analytical parameters were validated for the quantitative SPME-GC-MS-analysis as follows:

- *Linearity* was determined over 8 concentration levels from 0.5 to 100 ng L⁻¹.
- The *method detection and quantification limits* were determined through the signal to noise ratio at 1 ng L⁻¹ and 10 ng L⁻¹. The detection limit is defined as a signal to noise ratio of 3. Consistently, the quantification limit is defined as a signal to noise ratio of 10.
- The *precision (repeatability)* of the method was determined through the relative standard deviation (RSD) of the four-fold analysis of 10 ng L⁻¹, 50 ng L⁻¹ and 100 ng L⁻¹ samples.
- The *accuracy (recovery)* of the method was determined by analysing spiked real water samples (water from the three investigated lakes without detectable T&O background) at concentrations of 10 ng L⁻¹ and 100 ng L⁻¹.

More information on standard analytical parameters and extensive description of method validation for targeted SPME-GC-MS analysis of T&O compounds can be found in the literature [14, 15].

2.3 Results and discussion

2.3.1 Analytical method

Figure 2-1 exemplifies the result of a SPME-GC-MS/ODP-analysis. The chromatograms were obtained by analyzing a spiked MilliQ-water sample which contained eight T&O compounds at a level of $1 \mu\text{g L}^{-1}$. The upper chromatogram shows the signal (total ion current) of the MS, which was run in the scan mode from 50 to 400 m/z. The lower chromatogram shows sensory detections at the sniff-port.

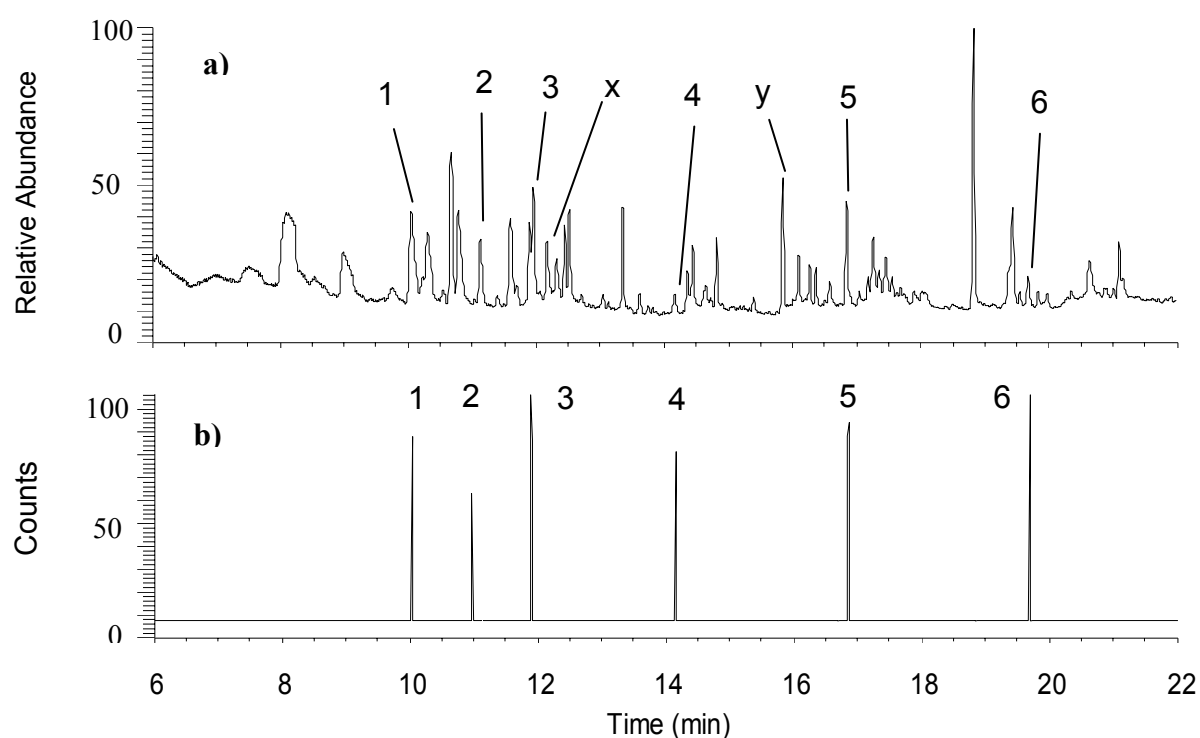


Figure 2-1: Chromatogram of a standard solution ($1 \mu\text{g L}^{-1}$ in MilliQ-water) analyzed with SPME-GC-MS/ODP. a) MS-chromatogram (total ion current in the scan-mode (50-400 m/z)), b) ODP-signal (“sniff-port”). Detected compounds (in brackets: the detected odor at the ODP): 1) 2-isopropyl-3-methoxypyrazine (decaying), 2) 2,6-nonadienal (cucumber), 3) 2-methyl-isoborneol (musty), 4) 2,4,6-trichloroanisole (musty), 5) β -ionone (violets), 6) 2,4,6-tribromoanisole (musty); x) β -cyclocitral, y) geosmin

It can be seen that the retention times of the two chromatograms shown in Figure 2-1 match perfectly. This is an important pre-requisite for the MS-identification of compounds which could be detected at the sniff-port. However, two of the eight compounds could only be detected with the MS (β -cyclocitral and geosmin). In the case of β -cyclocitral, this finding can be explained by its relatively high odor threshold (Table 2-1), which is above the spiked

concentration. The missing sensory detection of geosmin, which exhibits a low odor threshold of 4 ng L^{-1} (Table 2-1), is at the first glance surprising. However, this example illustrates the highly individual perception of odors. Reported odor threshold values sometimes vary over several orders of magnitude. The range in the public is expected to be even higher, because literature values are often the result from extensive studies with trained specialists. The $1 \text{ } \mu\text{g L}^{-1}$ -sample shown in Figure 2-1 was analyzed by three test persons. One could not detect geosmin at the sniff-port, whereas the others could easily detect it. In contrast, these two people were less sensitive or even totally lacked olfactory sensations towards other T&O compounds. Therefore, a water sample with unknown composition should be analysed by more than one person to ensure the sensory detection of all the relevant T&O compounds.

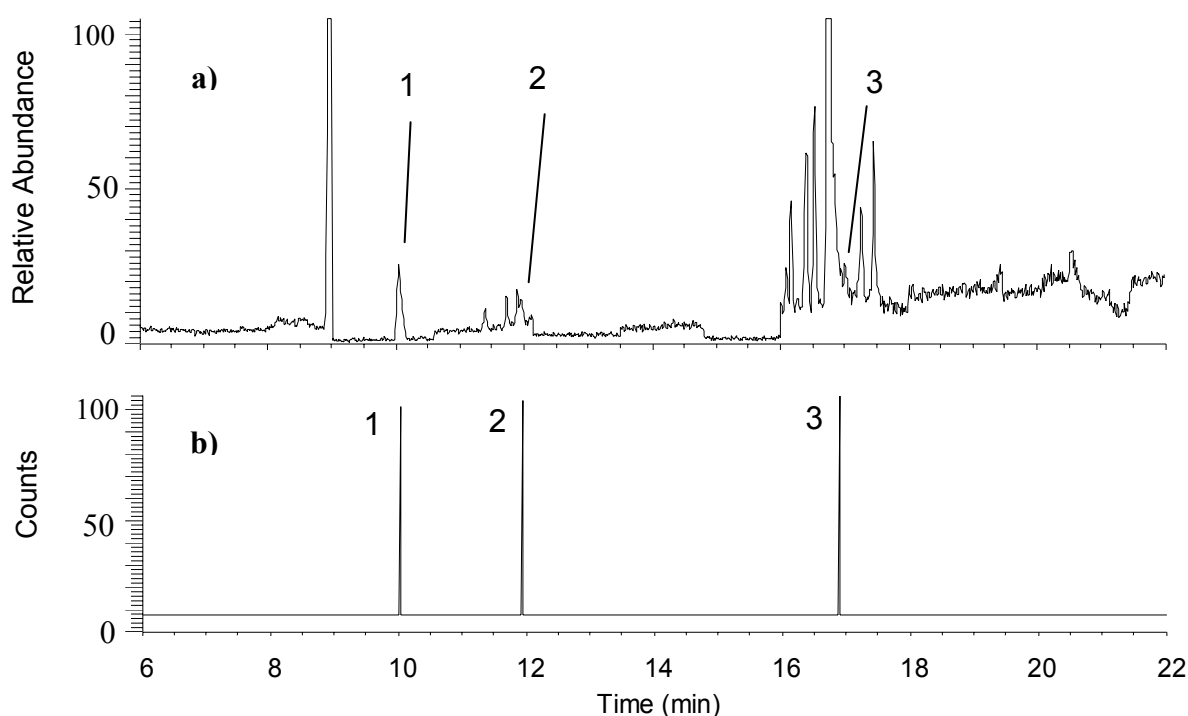


Figure 2-2: Chromatogram of a sample analyzed with SPME-GC-MS/ODP (composite sample of Lake Zurich, 7 June 2006, particle-bound fraction). a) MS-chromatogram (total ion current of the MS in the single ion mode), b) ODP-signal (“sniff-port”). Detected compounds (in brackets: the detected odor at the ODP): 1) 2-isopropyl-3-methoxypyrazine (decaying), 2) 2-methyl-isoborneol (musty), 3) β -ionone (violets)

Figure 2-2 illustrates the result for one of the lake samples analyzed in this study. Among the three T&O compounds found in this sample, only 2-isopropyl-3-methoxypyrazine could easily be detected with mass-spectrometry due to its relatively high concentration (5 ng L^{-1}). The other two compounds were present at lower concentrations and their peaks overlapped by neighboring peaks. Without the information from the ODP, a reliable detection of MIB and β -

ionone would not have been possible although the MS was run in the single ion mode in this case.

Method validation

MS detection limits for the analysis of the target compounds were in the sub to low ppt-range (Table 2-1). The lowest detection limits were achieved for MIB and IPMP. Even lower detection limits could be obtained at the ODP for compounds with very low odor thresholds. The analysis of spiked samples with concentrations $< 0.5 \text{ ng L}^{-1}$ did not lead to a response at the MS, but IPMP, MIB and TCA could still be perceived at the ODP.

Linearity for the quantitative MS analysis was excellent for the majority of the target compounds in a range of 2 - 100 ng L^{-1} . Additionally, the method showed good precision and accuracy. The relative standard deviation of the multiple analysis of spiked samples was within a range of 1 – 12 %. The recovery of the target compounds from the investigated natural waters was between 80% and 115%. The analytical parameters of the presented method are in good agreement with the SPME-GC-MS literature [14, 15].

SPME fiber lifetime

The lifetime of SPME-fibers was typically in the range of 100 extractions. However, artefacts of TCA and TBA could eventually be observed when several samples with concentrations above 50 ng L^{-1} were analysed. A longer desorption time in the injector (5 minutes) and a regular re-conditioning of the SPME fibers in methanol could mitigate this problem.

Method limitations

It should be noted that a few T&O compounds (such as the grassy compound 3-hexen-1-ol or the fishy 1-penten-3-one) could not be analysed with the presented method. This might be due to insufficient SPME extraction because of their polarity and potential hydrolysis at 65°C or due to decomposition in the hot split/splitless-injector. The latter could be minimized by the use of a PTV-injector (programmable temperature vaporizer) as proposed in ref. [15].

2.3.2 Application 1: T&O compounds in Swiss lake waters

Most of the T&O problems reported in the drinking water literature can be attributed to T&O compounds which are generated by algae and bacteria in surface waters [3]. The two most abundant T&O compounds in this context are geosmin and 2-methylisoborneol (MIB). However, several other semi-volatiles which are produced by aquatic micro-organisms can lead to T&O problems in the drinking water if inadequate water treatment is applied. It is therefore essential for water utilities which treat surface water to screen the raw water for any T&O compounds to get information about their concentration and their occurrence. With this knowledge, the drinking water treatment can be adjusted during periods of high T&O concentrations in the raw water. In this context, it is essential to analyse both the dissolved and intracellular fraction of T&O compounds. The latter can be an important source of T&O problems when particle-bound compounds are released from damaged cells of algae and bacteria during drinking water treatment.

In this study, three Swiss lakes with different nutrient levels were investigated on a monthly basis during half a year (Table 2-2). In Switzerland, approximately 20% of the drinking water is generated from lake waters. This percentage can be significantly higher in some of the major cities, e.g. 70% in Zurich, the largest city in Switzerland.

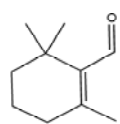
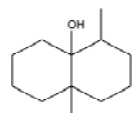
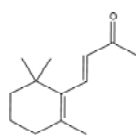
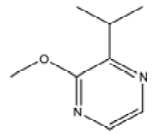
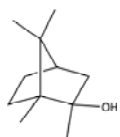
TABLE 2-2. Investigated lakes in application 1

	Lake Lucerne	Lake Zurich	Lake Greifensee
Degree of eutrophication	oligotrophic	mesotrophic	eutrophic
Surface area (km ²)	113.6	88.7	8.4
Maximum depth (m)	214	143	34
Lake stratification	March - December	March - December	March - December
pH	8.0	8.0	8.0
DOC (mg L ⁻¹)	0.9	1.2	3.7
Alkalinity (mM)	2.0	2.6	3.9
Sampling depths (m)	2; 10; 40	2.5; 12.5; 30	2.5; 10; 20

Table 2-3 shows the major findings of the lake survey. The data clearly reveal that in addition to the frequently found compounds, geosmin and MIB, other potent T&O compounds were present in the lake waters. Yet, the concentrations of the T&O compounds were rather low in the investigated lakes. Generally, the highest concentrations of both the dissolved and intracellular fraction were found in the epilimnion during summer concurrent with a high

phytoplankton biomass. Consistently, the concentration levels for certain compounds varied substantially between the three lakes and generally decreased in the order eutrophic Lake Greifensee > mesotrophic Lake Zurich > oligotrophic Lake Lucerne. It should be noted that the quantification limits for the particle-bound T&O compounds were approximately 30 times lower than for the dissolved compounds (Table 2-1) due to the enrichment factor through filtration. This explains the reliable quantification of β -ionone and MIB despite their low concentrations. β -ionone is the only identified T&O compound with a concentration peak in the metalimnion, i.e., at a depth of 10 to 15 m. Additionally, the highest concentrations of this compound were measured in fall, whereas all the other identified compounds exhibited earlier peak concentrations. The reason for this different spatial and temporal pattern of β -ionone can probably be explained by that fact that it is produced by bacteria which are most abundant during fall (*Planktothrix rubescens*). *Planktothrix* bacteria can grow at relatively low light intensities and therefore multiply in the metalimnion in fall, where light intensities have become insufficient for other species to grow. Detailed results of this survey are presented in Chapter 3.

TABLE 2-3. T&O Compounds identified in three Swiss lakes with peak concentrations (ng L⁻¹)

compound	structure	Lake Lucerne	Lake Zurich	Lake Greifensee	peak season
β -cyclocitral		1.3 ± 0.4 (d) ^a	2.7 ± 0.4 (d)	6.6 ± 0.4 (d)	summer
geosmin		1.5 ± 0.6 (d)	5.7 ± 0.6 (d)	19.0 ± 0.7 (d)	summer
β -ionone		0.3 ± 0.1 (p)	7.1 ± 0.1 (p)	1.6 ± 0.1 (p)	summer / fall
2-isopropyl-3-methoxypyrazine (IPMP)		10.0 ± 0.3 (p)	14.7 ± 0.5 (p)	16.1 ± 0.5 (p)	summer
2-methylisoborneol (MIB)		1.3 ± 0.1 (p)	2.6 ± 0.1 (p)	2.7 ± 0.1 (p)	summer

^a Errors = 95% confidence intervals, calculated from the calibration with six external standards
in brackets: d = dissolved; p = particulate fraction

2.3.3 Application 2: Musty odor in drinking waters

Due to changes in operation, the water utility in a town at the shore of Lake Zurich (Switzerland) was confronted with several consumers who complained about a musty odor in their drinking water. The complaints declined over time, but a few consumers kept complaining for more than a year. As a consequence of the complaints, samples taken at various places in the distribution system and at the tap were analyzed by a sensory panel. A musty odor was confirmed for some samples. However, they were restricted to a few households, whereas the water had a normal taste in other parts of the distribution system. Subsequently, water samples from the source to the tap (Fig. 2-3) were analyzed with SPME-GC-MS/ODP. Very small concentrations (below the quantification limit) of musty 2-methylisoborneol were detected in the lake water, but no indication of the musty odor was found in later treatment steps (Table 2-4). It can be expected that the concentrations of T&O compounds are reduced by at least 50% during ozonation and the subsequent activated carbon filtration (Chapter 4). Hence, it was obvious that the compound which led to the musty odor was formed in the distribution system and was not a problem of insufficient treatment of the lake water. To further investigate this finding, tap water samples were collected from the homes of consumers who complained about the musty taste (Fig. 2-3). The combined instrumental and organoleptic analysis clearly revealed that 2,4,6-trichloroanisole (TCA) was present in these tap water samples. TCA is a prominent T&O compound with a very low odor threshold ($<100 \text{ pg L}^{-1}$ [20]). TCA can be formed in the distribution system through a biomethylation of chlorophenols [21].

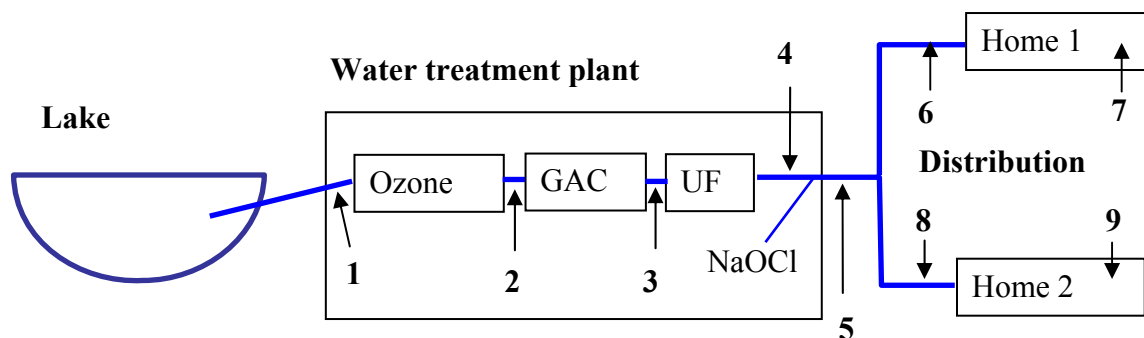


Figure 2-3: Sampling points in application 2 (GAC: granular activated carbon; UF: ultrafiltration membrane; NaOCl: sodium hypochlorite)

TCA was found at rather high concentrations in home 1, but was missing in the water sample collected from a hydrant in its vicinity (Fig. 2-3 and Table 2-4). Home 1 uses a particle filter in its house installation. This filter was covered with a biofilm at the time of the sampling campaign and could be the place where the formation of TCA occurred. In contrast, the water samples from home 2 and a hydrant in its vicinity both showed the same concentrations, which means that TCA was already present in the distribution system before home 2. A possible explanation of this finding is that home 2 was located at a dead end of the distribution system where the water throughput is low, which gives biofilms enough time to form TCA.

As a solution to this problem, the water utility decided to stop the addition of sodium hypochlorite to the treated water and hence reduce the concentration of precursors (chlorophenols) that could lead to TCA-formation. This measure proofed to be successful with respect to declining consumer complaints and reduced TCA concentration in the drinking water. Furthermore, the lacking residual disinfectant did not lead to higher bacterial growth in the distribution system. However, such an approach can only be taken if accompanied by careful monitoring and in an intact distribution system. Detailed results of this case study are presented in Chapter 6.

TABLE 2-4. Concentrations of T&O compounds determined in application 2, in ng L⁻¹ ^a

sampling point ^b	TCA	MIB
1 lake water	n.d. ^c	< 2 ^d
2 after ozonation	n.d. ^c	n.d. ^c
3 after GAC	n.d. ^c	n.d. ^c
4 after ultrafiltration	n.d. ^c	n.d. ^c
5 after NaOCl addition	n.d. ^c	n.d. ^c
6 hydrant home 1	n.d. ^c	n.d. ^c
7 tap water home 1	23.6 ± 2.8	n.d. ^c
8 hydrant home 2	6.4 ± 2.9	n.d. ^c
9 tap water home 2	4.9 ± 3.0	n.d. ^c

^a errors = 95% confidence intervals calculated from the calibration with five external standards

^b Fig. 2-3

^c n.d. = not detectable

^d MIB detected, but concentration below quantification limit

2.4 Conclusions

The most relevant T&O compounds with respect to consumer complaints in drinking water could be successfully analysed with the presented method. Detection limits for most of the investigated compounds were in the low ng L⁻¹-range with good linearity over two orders of magnitude. With its good accuracy and precision the presented method can also be applied to analyse T&O compounds in real water samples. Hence, the method with its parallel detection at the MS and the sniff-port allows a fast and reliable detection and quantification of T&O compounds in water samples. It should be noted, however, that sensory analysis is a very subjective method even in combination with MS detection. As discussed above, water samples with unknown composition should therefore be analysed by several persons to ensure the sensory detection of all the relevant T&O compounds.

The data of the lake survey (application 1) show the potential of the presented method. A reliable identification of the T&O compounds without a combined instrumental and sensory analysis would not have been possible because some of the compounds were only identified by the olfactory system. Additionally, the selectivity of headspace SPME toward volatile compounds proofed to be adequate for the sensitive analysis of T&O compounds in real water samples. The superiority of headspace SPME toward other extraction techniques is particularly pronounced for the analysis of T&O compounds in complex matrices such as the intracellular fraction of algae and bacteria.

Application 2 showed that the presented method with its parallel detection is also convenient to track the responsible compounds in drinking water after consumer complaints. However, even without sensory analysis, the targeted screening for the most relevant T&O compounds (Table 2-1) with a sample throughput of approximately 30 samples per day allows a fast screening of the occurrence of T&O compounds from the source to the tap. It is important to note that it is not possible to give general recommendations about the mitigation of T&O problems because specific solutions have to be found for each case. However, if the T&O origin can be localized and quantitative information of the involved compounds can be gained, well-designed counter-measures can be applied.

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Chapter 3

Field study (lake survey)

Occurrence of Dissolved and Particle-bound Taste and Odor

Compounds in Swiss Lake Waters

Abstract

The occurrence of dissolved and particle-bound taste and odor (T&O) compounds was investigated in three Swiss lakes which exhibit different nutrient levels from eutrophic to oligotrophic (Lake Greifensee, Lake Zurich and Lake Lucerne). In addition to the prominent T&O compounds geosmin and 2-methylisoborneol (MIB), four other T&O compounds could be detected in the lake waters, though all at relatively low concentrations (maximum concentrations of geosmin 19 ng L⁻¹, MIB 3 ng L⁻¹, β -ionone 27 ng L⁻¹, β -cyclocitral 7 ng L⁻¹, 2-isobutyl-3-methoxypyrazine 2 ng L⁻¹, 2-isopropyl-3-methoxypyrazine 16 ng L⁻¹). The concentration peaks typically occurred in the epilimnion during summer concurrent with a high phytoplankton biomass. Consistently, the concentration levels for most of the compounds varied substantially between the three lakes and generally decreased in the order eutrophic Lake Greifensee > mesotrophic Lake Zurich > oligotrophic Lake Lucerne. Furthermore, our data revealed that the occurrence of β -ionone was largely influenced by *Planktothrix rubescens*. This is the first time that a correlation between β -ionone and this cyanobacterium in natural waters has been reported.

3.1 Introduction

Surface waters are an important source for drinking water throughout the world. Some of the major cities in the world depend to a large degree on reservoirs, natural lakes or river bank filtration to obtain their drinking water. Normally, surface water has to be treated in a multi-step procedure consisting of particle separation and oxidation steps to fulfill the requirements with respect to microbiological quality, toxic compounds and aesthetic aspects such as color or taste and odor (T&O). Despite this enhanced water treatment, many water utilities are confronted with T&O complaints [1]. On the one hand, this is due to the very low odor thresholds of some T&O compounds (low ppt-range). On the other hand, drinking water treatment is often insufficient with respect to T&O removal. The resulting negative perception of the drinking water quality by the public can lead to a lack of trust in the water industry. Therefore, the water utilities are anxious to quickly and efficiently mitigate T&O problems. Most of the T&O compounds which lead to consumer complaints are formed in surface waters as metabolic products of micro-organisms [2, 3]. Generally, there are two possibilities for water utilities to handle this kind of T&O compounds. As a first option, the production of T&O compounds can be controlled at the source. This means that the growth of algae and bacteria in surface waters has to be limited. To reach this goal, copper-containing algicides such as copper sulfate have been applied successfully [4, 5]. However, while it is feasible to control algae in smaller reservoirs, it is difficult to control microbial growth in larger reservoirs, where tons of algicide are needed to affect algal blooms. Furthermore, the application of algicides often involves negative side-effects, which might become a long-term problem because most of the copper is accumulated in the sediments, which might release copper when the water chemistry changes [6]. These side-effects include the potential release of intracellular T&O compounds and cyanotoxins as well as negative effects on the aquatic life. As a second option, drinking water treatment could be optimized with respect to T&O removal (Chapters 4 and 5). However, an enhanced removal of T&O compounds can only be achieved to an economically feasible degree if the T&O compounds, their origins and their seasonal fluctuations are known. Therefore, it is important to screen the surface waters for any compound that could impart a bad taste or odor. In this context, special attention has to be paid to the analysis of dissolved as well as particle-bound T&O compounds. The latter can be an important source of T&O problems when particle-bound compounds are released from damaged cells of algae and bacteria during drinking water treatment.

Previous studies have mainly focussed on the production of T&O compounds by isolated species of algae and bacteria [7-10] or on the natural occurrence of selected T&O compounds (e.g. [11, 12]). With a more general approach, the authors of an earlier study attempted to comprehensively assess the volatile organic compounds (VOCs) in a eutrophic water body with GC-MS detection and correlate them with phytoplankton species [13]. However, this procedure does not allow a specific screening for T&O compounds that could be relevant to drinking water utilities. On the one hand, many VOCs do not change the organoleptic quality of the water because their concentrations are much lower than their respective odor threshold concentrations. On the other hand, potent T&O compounds, which are often present at trace levels, are likely to be missed in the analysis when their weak signals are overlapped by the background of the matrix.

The goal of this study was to identify all the T&O compounds of relevance for water utilities in three Swiss lakes, i.e., compounds that are present in the water at relevant concentrations for the human perception. To reach this goal and to assess the seasonal and spatial fluctuations of these compounds, a method that combined instrumental and sensory detection was applied (Chapter 2). Furthermore, this study aimed to verify whether the management of water bodies in Switzerland, i.e., the reduction of the nutrient load into surface waters, exhibited positive effects with respect to the occurrence of T&O compounds.

3.2 Materials and Methods

3.2.1 Chemicals and water

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 $\mu\text{g L}^{-1}$) were prepared in MilliQ-water. Sodium chloride, which was applied to enhance the extraction of the T&O compounds (see below) was reagent grade and used without further purification.

Water samples from three Swiss lakes (Lake Greifensee (10 km northeast of Zurich), Lake Zurich and Lake Lucerne) were screened for T&O compounds. Table 3-1 summarizes some characteristics of the investigated lakes.

TABLE 3-1. Characteristics of the investigated lakes and sampling schedule

	Lake Lucerne	Lake Zurich	Lake Greifensee
Trophic state	oligotrophic	mesotrophic	eutrophic
Surface area (km^2)	113.6	88.7	8.4
Maximum depth (m)	214	143	34
Lake stratification ^a	March - December	March - December	March - December
pH ^b	8.0	8.0	8.0
DOC (mg L^{-1}) ^b	0.9	1.2	3.7
Alkalinity (mM) ^b	2.0	2.6	3.9
Sampling depths (m)	2; 10; 40	2.5; 12.5; 30	2.5; 10; 20
Sampling schedule	05/06 and 06/06	03/06; 04/06; 05/06; 06/06; 07/06; 09/06 07/07; 08/07; 09/07; 10/07	03/06; 05/06; 06/06; 07/06

^a approximate period; might be prolonged or shortened depending on weather conditions in winter and late fall

^b mean value; subject to small fluctuations

3.2.2 Sampling and sample preparation

A detailed sampling schedule can be found in Table 3-1. A first sampling campaign of Swiss lake waters was performed in 2006 (March – September). The water samples (1 L) were taken from each the epilimnion, the metalimnion and the hypolimnion at fixed depths. In addition, vertical temperature profiles and phytoplankton data were recorded. For the latter,

phytoplankton species were determined and counted under microscopy in the laboratory of the water utility of Zurich.

An extensive description of the sample preparation is given in Chapter 2. Briefly, the samples were filtered immediately upon arrival and divided into a dissolved and a particle-bound fraction. The filter residue with the particle-bound fraction was re-suspended and the cells broken through the application of bead beating. After sample preparation, all the samples were stored in the dark at 4°C. For the analysis, sodium chloride (20% w/w) was added to all samples to enhance the transfer of the compounds into the gas phase. 2-isobutyl-3-methoxypyrazine (IBMP) was used as internal standard for the quantitative analysis and added at a concentration of 10 ng L⁻¹.

A second sampling campaign was performed at Lake Zurich from July to October 2007. The aim of this additional investigation was to reproduce a finding of the first campaign. Towards this end, lake water samples were taken from Lake Zurich as described above. Additionally, a 10 L sample was withdrawn from the metalimnion (12.5 m). Instead of a 0.45 µm filter, a filter with a larger pore size (8 µm; Sartorius, Germany) was used for this sample. This filter selectively retained *Planktothrix rubescens*, which form large colonies of several hundred cells in the water matrix. The filter residue, which mainly consisted of a thick layer of *Planktothrix rubescens*, was then carefully rinsed from the filter paper with 3 mL MilliQ water. For the verification of *Planktothrix rubescens* in the re-suspended residue, an aliquot of the samples was analyzed under a fluorescence microscope (Olympus BH-2 RFCA) using bluelight (495 nm) excitation. The subsequent bead-beating of the re-suspended residue was performed as described in Chapter 2.

3.2.3 Analysis of T&O compounds

The analytical method combined classical GC-MS detection with a simultaneous detection at an olfactory detector port (ODP). A detailed description of the method is given in Chapter 2. Briefly, the T&O compounds were extracted with head-space SPME (solid phase micro extraction) and then desorbed into a gas-chromatograph. The gas flow was split after the main GC column to make a simultaneous detection at the MS and at the ODP possible.

For the qualitative analysis, the ODP was coupled to an ion trap MS (GCQ, Thermo, Austin (TX), USA). After screening for off-flavours and identification of T&O compounds at the ODP and the MS, the sample was injected on another instrument (GC 8000 coupled to a

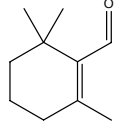
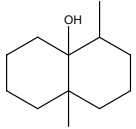
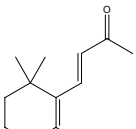
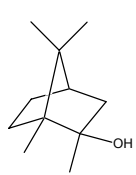
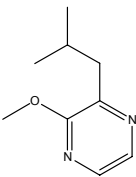
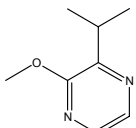
MD800, Fisons Instruments) for quantitative analysis with the MS in the single ion mode (SIM). The reason behind this instrument switch was that the quadrupole MS (MD800) gave better quantitative results than the ion trap MS used for the T&O-screening (for detailed method validation see Chapter 2). The settings for the SPME extraction and the GC separation were the same as described in Chapter 2, except for the lower head pressure (constant pressure at 50 kPa) due to the missing ODP.

3.3 Results and Discussion

3.3.1 Identified T&O compounds

Table 3-2 gives an overview of the eight compounds which were found in the investigated lakes.

TABLE 3-2. Taste and odor compounds detected in the three investigated lakes

compound	structure	odor	odor threshold (ng L ⁻¹)
β -cyclocitral		fruity	19000 [10]
geosmin		earthy	4 [14]
β -ionone		violets	7 [10]
2-methylisoborneol (MIB)		musty	15 [14]
2-isobutyl-3-methoxypyrazine		vegetable	1 [14]
2-isopropyl-3-methoxypyrazine		decaying vegetation	0.2 [14]

In the following section, the spatial and temporal pattern of the identified compounds is described in detail. Results are mainly presented from Lake Zurich and Lake Greifensee. There were too few samples out of Lake Lucerne and generally too low T&O concentrations to allow conclusions on seasonal dynamics of T&O compounds in Lake Lucerne. Nevertheless, the T&O compounds identified in Lake Lucerne were the same that were found in the other two lakes.

3.3.2 2-isobutyl-3-methoxypyrazine (IBMP)

IBMP was used as an internal standard for the analysis at a level of 10 ng L^{-1} (Chapter 2). However, IBMP was also present as a natural background in some of the particle-bound samples. Although a reliable quantification of the natural IBMP was not possible due to the lacking calibration and the influence of the spiked IBMP, the concentrations were generally around 1 ng L^{-1} and never exceeded 2 ng L^{-1} . IBMP has already been identified in natural waters in a previous study, where IBMP was described to be formed during the microbial degradation of grass under anaerobic conditions [15]. Hence, it remains unclear whether IBMP was actually present in the water by the time of sampling or was eventually formed during storage as a product of the decomposition of the algal biomass under microbiological activity. In contrast to the particle-bound fraction, IBMP could not be detected in the aqueous phase.

The fact that IBMP was present in some samples before the addition of the internal standard also affected the quantification of the other T&O compounds in these samples. Already small particle-bound concentrations can increase the IBMP signal due to the enrichment by approximately a factor of 30 during sample filtration (Chapter 2). In these cases, the quantification was performed with the calibration of external standards alone, i.e., without internal standard correction. Because of the very stable signal intensities, the analytical performance, e.g., linearity and precision, were not influenced significantly by this measure. Consistently, the estimated error for the data analysis without internal standard was in the same range as with internal standard correction (1 – 12 % (Chapter 2)).

3.3.3 2-isopropyl-3-methoxypyrazine (IPMP)

IPMP has been found in many food and water samples with vegetable to decaying odours [15]. It is known to be a product of soil organisms (actinomycetes). Additionally, it can probably be formed like IBMP through secondary microbiological processes [15] or even chemical processes during extraction steps at elevated temperature [8]. Hence, as in the case of IBMP it might be difficult to clearly track the origin of IPMP and refer absolute concentrations to natural occurrence or secondary processes during storage or analysis.

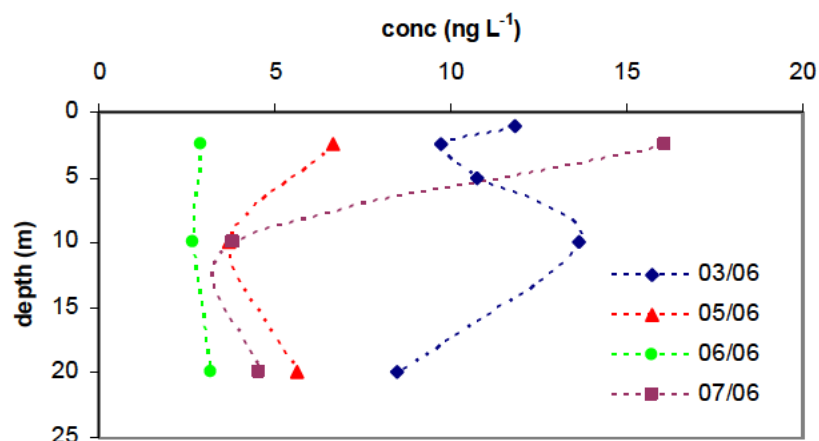


Figure 3-1: Concentration profiles of particle-bound IPMP in Lake Greifensee 2006.

In this study, IPMP was found in all particle-bound samples at rather high concentrations (3 – 16 ng/L), but never in the dissolved fraction during the sampling campaign in 2006. Particle-bound IPMP showed a clear seasonal pattern in all three lakes. Figure 3-1 exemplifies this pattern for Lake Greifensee, which exhibited the highest IPMP concentrations. A substantial decrease of IPMP in the whole water column could be observed from March to June. This can probably be interpreted as a result of the clear water phase, which is typically occurring in late spring. This period is characterized by a dramatic decrease of the phytoplankton biomass caused by intensive grazing of zooplankton on algae and bacteria (Table 3-3). In July, a substantial increase of IPMP could be observed in the epilimnion, which consistently can be explained with the re-growth of the phytoplankton. Because this growth is limited to surface-near water levels and because the lake does not allow vertical water exchange during summer due to stratification (as shown with the temperature profiles in Figure 3-2), the IPMP concentrations at 10 m and 20 m remained at a low level.

However, while it is possible to make relative statements by comparing the different profiles, it is important to note that the absolute IPMP concentrations shown in Figure 3-1 can be misleading. The data presented in Figure 3-1 were all determined several months after sampling. As mentioned above, apart from its natural occurrence IPMP might also be a product of microbial activity during sample storage, i.e., the result of the decomposition of the algal biomass. Indeed, storage seems to have had an influence on IPMP concentrations in the lake samples. The multiple analysis of some samples right after lake sampling and several months afterwards indicated that the IPMP concentration could eventually increase by more than 100%. However, most of the samples which were analysed after the same procedure did not show an increase in IPMP concentrations. Although the total IPMP formation potential

remains unknown, it seems likely that after a certain period IPMP concentrations should remain constant because the formation is expected to be asymptotic. This secondary IPMP formation represents a process that is likely to occur in the natural environment. When dead cells accumulate at the bottom of lakes which exhibit anaerobic conditions it is probable that pyrazines such as IBMP or IPMP are formed under microbial degradation of the biomass. These processes constitute a potential source of dissolved methoxy-pyrazines in the lake waters.

In short, absolute IPMP concentrations should be interpreted carefully as this compound can not only be formed by bacteria, but probably also through other biological or chemical processes after sampling.

3.3.4 2-methyl-isoborneol (MIB)

MIB is one of the most prominent T&O compounds described in literature. MIB is found among a diversity of microorganisms, e.g., protozoa, terrestrial actinomycetes, fungi and phytoplankton [9]. Among phytoplankton, different cyanobacteria species have been identified in culture experiments as MIB-producers [16]. Nevertheless, the biological function of this potent T&O compound remains unknown, although it might be an intermediate of pigment production in cyanobacteria [17]. Therefore, the highest MIB concentrations can be expected near the air-water interface, where cyanobacteria have to adapt to high UV irradiation. Indeed, the highest MIB concentrations (sometimes more than 100 ng L⁻¹) are typically found in the epilimnion during summer [12].

The samples analyzed in this study did not show a seasonal or spatial trend. Although MIB was detected in most of the dissolved and particle-bound samples, the concentrations were rather low and did not exceed 3 ng L⁻¹. Differences in the microbial community and therefore lacking of potent MIB-producers, such as several species of *Oscillatoria* and *Phormidium* [9], might explain these low concentrations compared to some natural waters in the literature.

3.3.5 Geosmin

Together with MIB, geosmin represents the most important T&O compound in drinking waters. As for MIB, many different cyanobacteria species and other microorganisms have been identified as potential producers [9, 16]. It is known that the dynamics of geosmin production can vary among different species and sometimes even among strains of the same

species. Furthermore, some cyanobacteria excrete most of the geosmin during growth whereas other species retain a large intracellular pool [9].

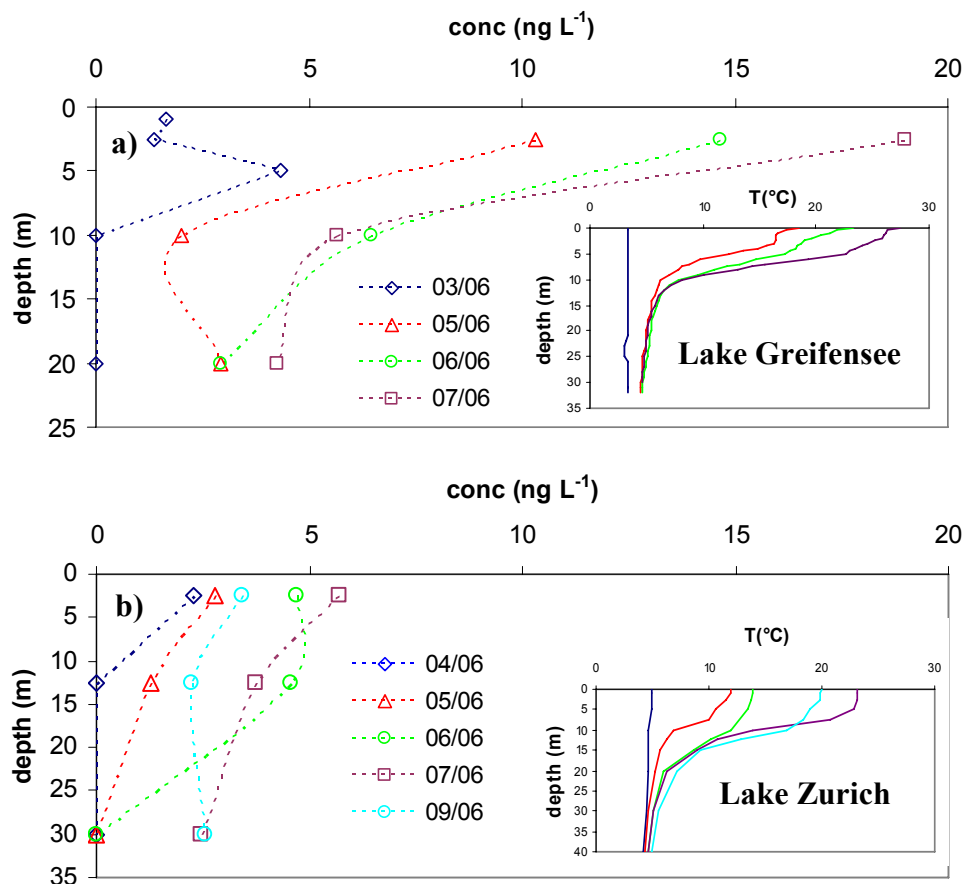


Figure 3-2: Concentration profiles of dissolved Geosmin in Lake Greifensee (a) and Lake Zurich (b) in 2006. The lines represent the corresponding temperature profiles.

In a previous study, the seasonal pattern of geosmin in Lake Zurich was investigated by Durrer and Jüttner [11]. The authors identified three main producers of geosmin in the lake water, namely the cyanobacteria *Aphanizomenon gracile* and to a lesser extent *Aphanizomenon flos-aquae* and *Oscillatoria limosa*.

In the present study, dissolved Geosmin was detected in all three lakes, although at different concentration-levels. Nutrient rich Lake Greifensee clearly exhibited the highest geosmin concentrations (maximum of 20 ng L^{-1}), followed by Lake Zurich (maximum of 6 ng L^{-1}) and oligotrophic Lake Lucerne (maximum of 2 ng L^{-1}). Figure 3-2 shows the increase in the epilimnion concentration from March to July in Lake Greifensee and Lake Zurich. The seasonal pattern of dissolved geosmin looks similar to the profiles that were measured by Durrer and Jüttner in Lake Zurich in 1996 [11]. In contradiction to that study, geosmin was not found in the particle-bound fraction. However, Durrer and Jüttner detected particle-bound

geosmin mainly at a depth of 1 m, which was not sampled in this study (Table 3-1). Furthermore, Durrer and Jüttner used methanol and a mortar to crunch the cells instead of bead beating. Yet, own experiments with this former method confirmed that the choice of the extraction procedure is not likely to lead to significantly different T&O signals. Apart from the different sampling points, differences in the geosmin pattern are probably due to a different composition of the microbial community driven by changed environmental conditions. Indeed, out of the three species that Durrer and Jüttner identified as main geosmin-producers in Lake Zurich in 1996, only small numbers of *Aphanizomenon flos-aquae* were found ten years later (Table 3-3). *Aphanizomenon gracile* and *Oscillatoria limosa* have disappeared completely.

3.3.6 *β-cyclocitral*

The nor-carotenoid *β-cyclocitral* has been detected at high concentrations in eutrophic water bodies in earlier studies [8, 13]. *Microcystis* cyanobacteria have been reported as the major producers of this T&O compound [9].

In this study, *β-cyclocitral* was mainly found in the dissolved fraction. It should be noted that the identification of this compound was only possible because the samples were analysed specifically for *β-cyclocitral* with the MS in the SIM-mode (Chapter 2). Due to its high odor threshold of 19 µg L⁻¹ (Table 3-2), *β-cyclocitral* could not be detected at the ODP. In all three lakes, *β-cyclocitral* showed a certain seasonal pattern, which can best be seen in Lake Greifensee (Figure 3-3). The highest concentrations were found in the epilimnion in July concurrent with a high density of phytoplankton. The seasonal pattern of *β-cyclocitral* looks similar to geosmin, i.e., a large increase in the epilimnion concentration towards July. This might indicate that the same species were responsible for their respective production in the three lakes. However, a survey of cyanobacteria showed that none of the geosmin producing species was also capable of producing *β-cyclocitral* and vice versa [9]. Hence, it is likely that geosmin and *β-cyclocitral* were produced in the same assemblage of cyanobacteria, but not by the same species.

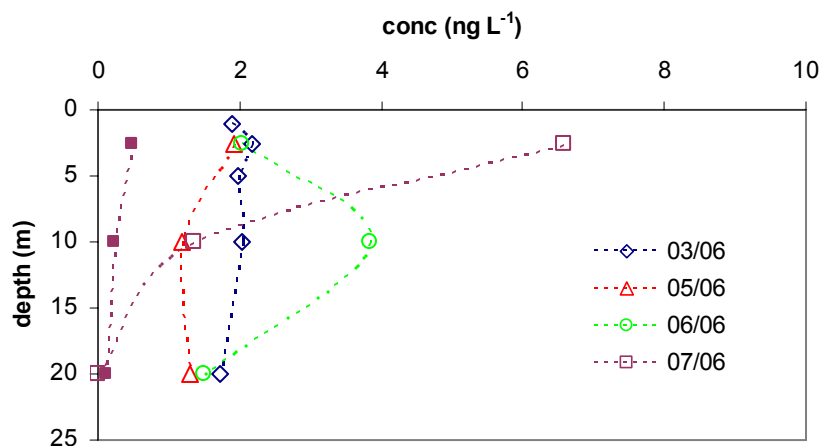


Figure 3-3: Concentration profiles of β -cyclocitral in Lake Greifensee 2006. Empty symbols represent the dissolved fraction, filled symbols the particle bound fraction

3.3.7 β -ionone

Like β -cyclocitral, β -ionone is a product of carotene oxidation [9]. Amongst its producers are different species of algae and cyanobacteria.

In this study, dissolved β -ionone could only be detected in some epilimnion and metalimnion samples of Lake Zurich (data not shown). In contrast, this compound was found in almost all particle-bound samples, though generally at very low concentrations ($<1 \text{ ng L}^{-1}$). An exceptionally high concentration was measured in the particle-bound sample of Lake Zurich which was taken from the metalimnion in September 2006 (Figure 3-4a). The two main β -ionone producers that were identified in an earlier study (*Cyanidium caldarium* and *Synura uvella* [8]) were not present in Lake Zurich water. However, this peak concentration coincided with an abundance of *Planktothrix rubescens* (former name: *Oscillatoria rubescens*), a red cyanobacterium that can form large colonies of hundreds of cells (Figure 3-5). This species is especially abundant in the metalimnion in late summer because its requirements for irradiation and temperature are low compared to other species [18]. Table 3-3 shows that not only the numbers of *Planktothrix rubescens* increased towards fall, but that this species also increased in size. The carotenoid pigments (myxoxanthin) in *Planktothrix rubescens* contain β -ionone rings that are conjugated with polyene chains [19]. Although this makes *Planktothrix rubescens* a likely β -ionone producer, such a correlation has not been reported for surface waters.

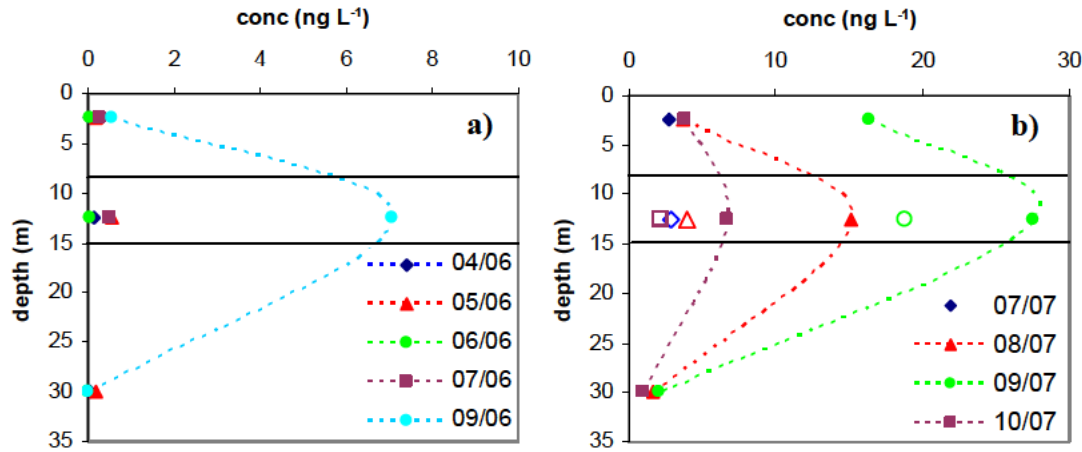


Figure 3-4: Concentration profiles of particle-bound β -ionone in Lake Zurich in 2006 (a) and 2007 (b). Filled symbols represent the total particle-bound fraction (0.45 μ m filtered); empty symbols represent the *Planktothrix rubescens* fraction (only 12.5m samples). The black lines indicate the thermocline (8 - 15m; Fig. 3-2b).

To further examine whether β -ionone was mainly produced by *Planktothrix rubescens* in Lake Zurich, an additional sampling campaign was run from July to October 2007. Special attention was paid to the metalimnion samples, out of which one was filtered as usually with a 0.45 μ m filter, which retained the whole phytoplankton community, whereas the other sample was filtered with an 8 μ m filter, which selectively retained *Planktothrix rubescens* (see method section for details). Figure 3-4b shows the results of this second sampling campaign. Firstly, it can be seen that the β -ionone concentrations in the metalimnion were even higher in September 2007 than in September 2006. Secondly, the role of *Planktothrix rubescens* as single producers of β -ionone increased from July to September. Like β -ionone, this cyanobacterium exhibited higher abundance in the metalimnion in September 2007 than in September 2006 (Table 3-3). In August 2007, where light intensities in the metalimnion were probably high enough for many other species to grow, *Planktothrix rubescens* contributed only a minor part to the observed total particle-bound β -ionone. The situation changed as light intensities decreased. In September, most of the particle-bound β -ionone was produced by *Planktothrix rubescens*. Furthermore, this species is likely to be responsible for the high β -ionone concentration in the epilimnion in September 2007 because its numbers show a large increase from August to September at 2.5 m (Table 3-3). Although *Planktothrix rubescens* was still abundant in the epilimnion and the metalimnion in October 2007, β -ionone concentrations were again as low as during most of the season. As β -ionone is related to carotene pigments, it is possible that reduced light intensities might explain the lower

concentrations in October. However, the environmental factors that govern the formation of β -ionone remain unclear.

TABLE 3-3. Phytoplankton as a function of depth in Lake Zurich in 2006 and 2007

Total Phytoplankton Biomass ($\mu\text{g L}^{-1}$)								
depth (m)	05/06	06/06	07/06	09/06	07/07	08/07	09/07	10/07
2.5	5449	845	4419	2582	2745	2123	3208	2626
12.5	3698	1101	5371	3207	3406	2125	3598	4109
30	1392	610	533	241	1459	265	328	361
Aphanizomenon flos-aquae (#/mL)								
depth (m)	05/06	06/06	07/06	09/06	07/07	08/07	09/07	10/07
2.5	0.9	5	n.d. ^a	1	0.4	0.2	3	0.4
12.5	1	7	11	15	10	2	1	0.4
30	0.2	0.2	n.d.	0.6	0.2	n.d.	n.d.	n.d.
Planktothrix rubescens (#/mL)								
depth (m)	05/06	06/06	07/06	09/06	07/07	08/07	09/07	10/07
2.5	19	n.d.	n.d.	9	5	0.6	117	85
12.5	64	30	11	163	145	153	259	330
30	51	13	4	0.2	8	7	13	17
Planktothrix rubescens (size in μm)								
depth (m)	05/06	06/06	07/06	09/06	07/07	08/07	09/07	10/07
2.5	335	n.d.	n.d.	210	n.a. ^b	265	530	695
12.5	470	190	550	605	n.a.	445	540	500
30	215	185	135	60	n.a.	245	370	305

^a n.d. = not detected; ^b n.a. = not available



Figure 3-5: Colonies of *Planktothrix rubescens* under a fluorescence microscope. Water sample from Lake Zurich (12.5 m) in July 2007 (8 μm filtered).

3.4 Conclusions

In the three lakes, a total of six different T&O compounds was detected. A general correlation to the phytoplankton biomass and therefore, elevated T&O concentrations in eutrophic water bodies has been confirmed in this study. Furthermore, the presented data set revealed that the occurrence of some T&O compounds can vary substantially from one year to another. In this context, β -ionone is of special interest because its correlation to the seasonal dynamics of the cyanobacterium *Planktothrix rubescens* has not been reported previously. However, there are still many open questions with respect to the origins of some of the other detected T&O compounds.

These six compounds are a fairly small fraction of the roughly 200 algal T&O compounds that have been described in the literature [9]. However, the aim of this study was to describe only T&O compounds that are present at relevant concentrations, i.e., compounds that could potentially lead to consumer complaints. Hence, it is likely that other T&O compounds could be found in the investigated lakes, though at concentrations well below their respective odor thresholds.

Even though the data of this study do not cover a full year and not all lakes, it seems unlikely that T&O problems in Switzerland could be generated by dissolved algal metabolites from lake waters. On the one hand, the concentrations of the identified compounds were generally very low already in the lake waters. On the other hand, a multi-barrier approach is standard for lake water treatment in Switzerland. During this treatment, T&O compounds are likely to be retained or oxidized by far more than 50% (Chapters 1 and 4). As for the particle-bound compounds, their removal or potential release during drinking water treatment is strongly dependent on the treatment processes, i.e., on the sequence of removal and oxidation processes. In the investigated lakes, though, the concentrations of particle-bound compounds are probably also too low to generate T&O problems.

These low T&O concentrations are an indicator for the good surface water quality in Switzerland and underline the efficacy of the measures that had been taken to minimize the nutrient loads into surface waters. However, as the phytoplankton community is subject to constant changes driven by environmental factors such as the nutrient availability or water temperature, it is difficult to predict the future algal T&O production. It is possible that concentrations of T&O compounds in the investigated lakes will rapidly increase if a particular species or even genotype is favored by future environmental conditions.

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Chapter 4

Ozonation of Taste and Odor Compounds

Peter, A.; von Gunten, U.: Oxidation kinetics of selected taste and odor compounds during ozonation of drinking water, *Environ. Sci. Technol.* **2007**, *41* (2), 626-631.

Abstract

The applicability of ozonation to mitigate taste and odor problems in drinking water was investigated. Second order rate constants of eleven taste and odor compounds with ozone and hydroxyl radicals were determined under laboratory conditions. Measured rate constants for the reaction with hydroxyl radicals are between $3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $10^{10} \text{ M}^{-1}\text{s}^{-1}$ and for ozone: $k_{\beta\text{-cyclocitral}} = 3890 \pm 140 \text{ M}^{-1}\text{s}^{-1}$; $k_{\text{geosmin}} = 0.10 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$; $k_{3\text{-hexen-1-ol}} = 5.4 \pm 0.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$; $k_{\beta\text{-ionone}} = 1.6 \pm 0.13 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$; $k_{2\text{-isopropyl-3-methoxypyrazine}} = 50 \pm 3 \text{ M}^{-1}\text{s}^{-1}$; $k_{2\text{-methylisoborneol}} = 0.35 \pm 0.06 \text{ M}^{-1}\text{s}^{-1}$; $k_{2,6\text{-nonadienal}} = 8.7 \pm 0.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$; $k_{1\text{-penten-3-one}} = 5.9 \pm 0.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; $k_{2,6\text{-di-tert-butyl-4-methylphenol (BHT)}} = 7.4 \pm 0.2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; $k_{2,4,6\text{-tribromoanisole}} = 0.02 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$; $k_{2,4,6\text{-trichloroanisole}} = 0.06 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$.

Experiments conducted in natural waters showed that the removal efficiency during ozonation can be reliably predicted with the determined second order rate constants. Ozonation is a powerful tool capable to oxidize most of the taste and odor compounds to more than 50% under typical drinking water treatment conditions. For ozone-resistant taste and odor compounds, the application of advanced oxidation processes may be appropriate.

4.1 Introduction

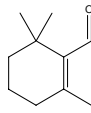
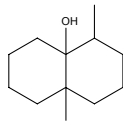
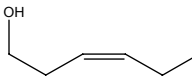
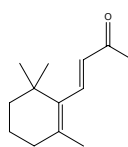
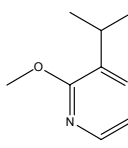
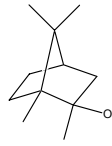
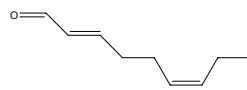
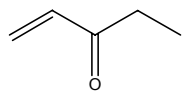
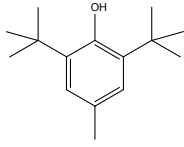
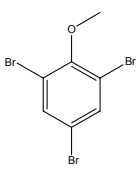
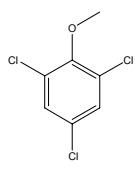
Taste and odor (T&O) episodes are the reason for most consumer complaints to water utilities. Even though in many cases T&O causing compounds do not pose a toxicological threat to humans, they affect the public's perception of the safety of drinking water [1]. This negative perception can lead to a lack of trust in the water industry.

It is difficult to control T&O compounds from a source point of view because most of them are of natural origin and are closely related to the growth and metabolism of algae and bacteria in surface waters [2]. However, T&O problems can be avoided or at least be minimized through an optimization of drinking water treatment processes. Towards this end, many water suppliers rely on chemical oxidation processes. It is evident from the literature that ozonation, which involves reactions with both ozone and hydroxyl radicals ($\cdot\text{OH}$), can be a very effective procedure for the removal of off-flavours with several advantages over the use of chlorine or chlorine dioxide [3].

Previous studies on the ozonation of T&O compounds were mostly empirical and have focussed on improving the technical processes and on determining the doses of ozone required to yield a certain removal efficiency [3]. However, the case-specific results of these studies often cannot be transferred to other water utilities which have to deal with a different raw water quality. Data on the kinetics of oxidation processes involving both ozone and $\cdot\text{OH}$ would provide a useful tool to optimize ozonation, which means ensuring an optimal removal of off-flavours and other contaminants concurrent with an adequate disinfection. Unfortunately, these data, i.e., accurate second order rate constants, are often lacking in literature. In a recent study, second order rate constants for geosmin and 2-methylisoborneol (MIB) – the two most prominent T&O compounds described in literature – for their reaction with ozone and $\cdot\text{OH}$ have been determined [4]. However, in the experimental setup of that study the ozone reaction pathway was not separated from the $\cdot\text{OH}$ reaction. The second order rate constants were determined by fitting the measured decrease of the reactants with a model, which resulted in rather high uncertainties. No other second-order rate constants for the reaction of T&O compounds with ozone or $\cdot\text{OH}$ could be found in literature.

We determined second order rate constants under laboratory conditions for the reaction of ozone and $\cdot\text{OH}$ with eleven relevant off-flavour compounds exhibiting a wide variety of molecular structures (Table 4-1). Additionally, we conducted experiments with lake water to determine the effect of the water matrix on the ozonation efficiency and to test the applicability of laboratory data on natural water systems.

TABLE 4-1. Taste and odor compounds selected for kinetic experiments

	compound (CAS number)	structure	odor	odor threshold (ng L ⁻¹)	source
natural compounds in surface waters (from algae or bacteria)	β -cyclocitral (432-25-7)		fruity	19000 [5]	cyanobacteria
	geosmin (16423-19-1)		earthy	4 [6]	cyanobacteria and actinomycetes
	cis-3-hexen-1-ol (928-96-1)		grassy	70000 [5]	algae
	β -ionone (79-77-6)		violets	7 [5]	algae, cyanobacteria
	2-isopropyl-3-methoxypyrazine (25773-40-4)		decaying vegetation	0.2 [6]	actinomycetes
	2-methylisoborneol (MIB) (2371-42-8)		musty	15 [6]	cyanobacteria and actinomycetes
	trans,cis-2,6-nonadienal (557-48-2)		cucumber	20 [7]	algae
	1-penten-3-one (1629-58-9)		fishy - rancid	1250 [5]	algae, cyanobacteria
various sources in distribution systems	2,6-di- <i>tert</i> -butyl-4-methylphenol (BHT) (128-37-0)		plastic	not available	leaching from polyethylene pipes
	2,4,6-tribromoanisole (TBA) (607-99-8)		earthy - musty	0.03 [8]	methylation of bromophenol by microorganisms
	2,4,6-trichloroanisole (TCA) (87-40-1)		musty	0.03 [8]	methylation of chlorophenol by microorganisms

4.2 Materials and Methods

4.2.1 Standards and Reagents

Geosmin and 2-methylisoborneol were purchased from Wako Chemicals (Osaka, Japan); all the other T&O compounds were obtained from Sigma-Aldrich (Buchs, Switzerland) in the highest purity available. Stock solutions (1 mM and 50 μ M, respectively, depending on the water solubility) were prepared in MilliQ-water. All chemicals used for solutions were reagent grade and were used without further purification.

2,6-di-*tert*-butyl-4-methylphenol (BHT) has a very low water solubility of approximately 1 mg L⁻¹ [9]. To achieve the desired concentration level for the BHT stock solutions, BHT was first dissolved in a co-solvent and then added to MilliQ-water. Acetonitrile was selected as co-solvent for the \cdot OH-experiments due to its low reactivity toward hydroxyl radicals ($k_{\text{OH,Acetonitrile}} = 2.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ [10]). The addition of Acetonitrile does affect the hydroxyl radical exposure, but not the calculation of the \cdot OH reaction rate constant because this constant was determined using competition kinetics (see below). For the ozone experiments, BHT was first dissolved in *tert*-butanol, which at the same time served as an \cdot OH-scavenger.

Ozone was produced from pure oxygen with a CMG 3-3 ozone generator (Apaco AG, Grellingen, Switzerland) and then transferred into an ice-cooled flask containing MilliQ-water. Concentrations in this stock solution were typically around 1.3 mM.

Raw waters from two Swiss lakes were used for the natural water experiments: (i) water from mesotrophic Lake Zurich, collected at a depth of 30 m, was obtained from Wasserversorgung Zürich (WVZ) (pH 7.9; DOC 1.2 mg L⁻¹; alkalinity 2.6 mM); (ii) water from eutrophic Lake Greifensee was sampled at a depth of 10 m in the middle of the lake (pH 8.1; DOC 3.7 mg L⁻¹; alkalinity 3.9 mM). The water samples were filtered immediately upon arrival (0.45 μ m cellulose nitrate filters) and stored in the dark at 4°C.

4.2.2 Analytical methods

Below, a brief overview of the applied analytical methods is given.

T&O compounds. All compounds were analysed using high-performance liquid chromatography (HPLC, Agilent 1100 series) with UV or MS/MS detection. Isocratic and gradient eluents consisted of methanol and MilliQ-water or 10-50 mM phosphoric acid buffer (pH 2.2), respectively. The column used was Nucleosil 100-5 C18 (Macherey Nagel, Oensingen, Switzerland). The flow rate was held constant at 1 mL min⁻¹ (0.4 mL min⁻¹ for geosmin and MIB) and the volume injected amounted to 100 µL (50 µL for geosmin and MIB).

Geosmin and MIB do not absorb UV light above 200 nm and had therefore to be detected by means of mass spectrometry. MS/MS was applied (Thermo, Finnigan LTQ) with atmospheric pressure chemical ionisation (APCI) in the positive ionization mode. Precursors used for fragmentation (MS/MS) were 165.1 for geosmin and 151.2 for MIB, respectively. The quantifier-product ions were 109.0 and 95.0 for geosmin and 81.0 and 95.0 for MIB, respectively. The other T&O compounds were detected through a diode-array detector (Agilent 1100 series) at or close to their UV-absorption maximum (between 200 and 310 nm). The detection limits achieved were < 0.1 µM (< 1 µM for geosmin). The method showed excellent linearity in the range of 0.3-50 µM (0.3-4 µM for BHT and 1-25 µM for geosmin).

Ozone. Dissolved ozone was analyzed using the Indigo method [11] or spectrophotometrically at 258 nm ($\epsilon = 3000 \text{ M}^{-1}\text{cm}^{-1}$) when there was no interference present in the reaction solution.

4.2.3 Determination of rate constants for the reaction of taste and odor compounds with hydroxyl radicals and ozone

The experimental setup was adapted from Huber et al [12]. In the following section, a short overview of the applied methods is given. Generally, the experiments were run in duplicates or triplicates.

Hydroxyl radicals ($\cdot\text{OH}$)

The reaction rate constants were determined by means of competition kinetics with pCBA (4-chlorobenzoic acid) as reference compound. $\cdot\text{OH}$ were generated either by photolysis of hydrogen peroxide (H_2O_2) at 313 nm in a merry-go-round photo reactor (DEMA model 125, Hans Mangel GmbH, Bornheim-Roisdorf, Germany) or with γ -radiolysis (type GAMMACELL, Atomic Energy of Canada; the dose rate for water amounted to approximately 1.4 kGyh^{-1} in the center of the ^{60}Co γ -radiation source with lead shielding) for compounds which undergo direct photolysis at wavelengths of $>300 \text{ nm}$. An overview of the methods applied for each compound is given in Table 4-2.

All experiments were carried out at pH 7 in 5 mM phosphate buffer. The temperature in the photoreactor was held constant at 25°C . Initial concentrations were 1-20 μM for the reactants and 1-40 mM for H_2O_2 . Total reaction time was one hour in the photoreactor and 500 seconds for γ -radiolysis. The irradiation was interrupted to withdraw several samples, which were analysed immediately with HPLC. To verify whether direct photolysis in the photo reactor occurred, a blank without addition of H_2O_2 was irradiated under the same experimental conditions.

The second order rate constants of the T&O compounds (P) were determined using eq 1 by plotting the decrease of P against the reference compound (R).

$$\ln\left(\frac{[P]}{[P]_0}\right) = \ln\left(\frac{[R]}{[R]_0}\right) \frac{k_{\text{OH},P}}{k_{\text{OH},R}} \quad (1)$$

The slope of the linear regression corresponds to the ratio $\frac{k_{\text{OH},P}}{k_{\text{OH},R}}$ of the second order rate constants of P and R for their reaction with OH radicals. This allows to calculate $k_{\text{OH},P}$ with

$k_{\text{OH}, \text{pCBA}} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [13]. The regression yielded also the uncertainty of the slope, which was propagated to $k_{\text{OH}, \text{P}}$.

Ozone

Slow reacting compounds ($k < 4000 \text{ M}^{-1}\text{s}^{-1}$). The second order rate constants were determined by following the decrease of the compound in presence of ozone in at least a ten-fold excess. The experiments were carried out in 250 mL glass bottles at 20-25°C and pH 2 (50 mM H_3PO_4), except for 2-isopropyl-3-methoxypyrazine (pH 5; 5 mM phosphate buffer) due to its pK_a value of 1.1. *Tert*-butyl alcohol (t-BuOH, 10-20 mM) was added as an $\cdot\text{OH}$ -scavenger in all experiments. An aliquot of the ozone stock solution was injected with a syringe to start the reaction. The initial ozone concentrations ranged from 15 to 700 μM depending on the expected reactivity of the compound toward ozone. Several 1 mL samples were withdrawn with a dispenser system [14] into HPLC vials, which contained fresh sodium sulfite solution (2-25 mM) to quench the ozone. The total reaction time varied from 90 s for β -cyclocitral to 270 min for 2,4,6-tribromoanisole and 2,4,6-trichloroanisole.

Ozone decomposition [15] had to be taken into account for experiments which were run for more than a few minutes. In these cases, the ozone exposure was determined by withdrawing additional samples for ozone analysis.

The concentrations of the T&O compounds were then plotted versus the ozone exposure.

$$\ln\left(\frac{[P]}{[P]_0}\right) = -k_{P, O_3} \int [O_3] dt \quad (2)$$

According to eq 2, the slope of the regression line of a plot of $\ln\left(\frac{[P]}{[P]_0}\right)$ vs $\int [O_3] dt$ directly represents the second order rate constant (k_{P, O_3}).

Fast reacting compounds ($k > 4000 \text{ M}^{-1}\text{s}^{-1}$). Competition kinetics was applied to determine the second order rate constants for the compounds showing high reactivity toward ozone. The target compound and a reference compound with a similar reaction rate constant (*trans*-cinnamic acid; $\text{pK}_a = 4.4$; $k_{O_3, \text{protonated species}} = 5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; $k_{O_3, \text{deprotonated species}} = 3.8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ [16]) were added to a 25 mL flask at the same initial concentration (5-50 μM). t-BuOH (10 mM) served as an $\cdot\text{OH}$ -scavenger. The pH was adjusted with phosphate buffer (5-50 mM)

to a value of 2 or 8 to yield the desired reactivity of the reference compound. Seven understoichiometric concentration levels of the ozone stock solution were injected into the reaction mixture. One minute after each injection a 1 mL sample was withdrawn. A control was run under the same conditions without adding ozone to check for the loss of the compounds through volatilization. Second order rate constants k_{O_3} were determined according to eq 1 by replacing k_{OH} with k_{O_3} .

Ozonation of natural waters

To assess the influence of the water matrix on the ozonation efficiency, experiments were performed in filtered water from Lake Zurich and Lake Greifensee at 20-25°C. T&O compounds were spiked at levels low enough to avoid significant changes in the ozone and hydroxyl radical exposure. The experiments were conducted with (i) three fast reacting compounds (β -cyclocitral, 2,6-nonadienal and 1-penten-3-one) and (ii) four slow reacting compounds, respectively (2-isopropyl-3-methoxy-pyrazine, geosmin, 2-methylisoborneol, 2,4,6-tribromoanisole):

(i) The aim was to investigate which ozone dose is needed for a certain removal efficiency of the fast reacting compounds. To this end, the filtered lake water was spiked with one T&O compound (0.5 μM) and then transferred into five 50 mL flasks. The solutions were vigorously stirred while ozone doses of 0.1, 0.2, 0.5, 1 and 2 mg L^{-1} were injected. After 15 min reaction time, which corresponds roughly to the residence time of water in an ozone reactor during drinking water treatment, the residual T&O concentrations were analysed with HPLC. Sodium sulfite (2.5 mM) was added at the end of the experiment to the solutions containing 1 mg L^{-1} and 2 mg L^{-1} of ozone to quench the residual ozone.

(ii) Experiments with slow reacting compounds were conducted to determine their half-life during ozonation and to check whether the degradation could be modelled with the previously determined second order rate constants. Filtered lake water was spiked with one T&O compound (0.5-1 μM ; 5 μM in the case of geosmin because of the higher detection limit) and pCBA (0.5 μM). pCBA served as an indicator of the $\cdot\text{OH}$ -exposure because it does not react with ozone directly [17]. After ozone had been injected (1 mg L^{-1} for Lake Zurich water and 2 mg L^{-1} for Lake Greifensee water), samples were withdrawn in regular intervals for the determination of the ozone exposure with the indigo method and for the analysis of the T&O compounds. In the latter case, the residual ozone was quenched by adding sodium sulfite.

4.3 Results and Discussion

4.3.1 Hydroxyl radicals ($\cdot\text{OH}$)

$\cdot\text{OH}$ – which are formed during ozone decomposition [17, 18] – are powerful electrophiles that typically react at nearly diffusion-controlled rates with organic compounds. In ozonation, $\cdot\text{OH}$ contribute a major part to the oxidation of micropollutants with electron-poor moieties, i.e., compounds with a low reactivity toward ozone. The measured second order rate constants for the reaction of the selected taste and odor compounds with $\cdot\text{OH}$ are summarized in Table 4-2.

During irradiation of the blank (without H_2O_2) in the photo reactor, 1-penten-3-one and 2,6-nonadienal were slightly degraded. This was probably due to direct photolysis although it was not expected regarding the low UV absorption of these compounds at 313 nm. Nonetheless, direct photolysis was taken into account for these two compounds and the observed reaction rate constant was corrected accordingly.

TABLE 4-2. Second order rate constants for the reaction of $\cdot\text{OH}$ with selected T&O compounds

Compound	Method	k ($10^9 \text{ M}^{-1}\text{s}^{-1}$)	σ ($10^9 \text{ M}^{-1}\text{s}^{-1}$) ^a
β -cyclocitral	UV/ H_2O_2	7.42	0.78
geosmin	UV/ H_2O_2	7.80	0.24
3-hexen-1-ol	UV/ H_2O_2 (γ -radiolysis)	7.45 (7.59)	0.55 (1.13)
β -ionone	γ -radiolysis	7.79	0.34
2-isopropyl-3-methoxypyrazine	γ -radiolysis	4.91	0.13
2-methylisoborneol	UV/ H_2O_2	5.09	0.14
2,6-nonadienal	UV/ H_2O_2 (γ -radiolysis)	10.49 ^b (8.95)	2.38 (0.61)
1-penten-3-one	UV/ H_2O_2	4.71 ^b	0.79
BHT	UV/ H_2O_2	3.20	1.95
2,4,6-tribromoanisole	γ -radiolysis	3.74	0.43
2,4,6-trichloroanisole	γ -radiolysis	5.10	0.11

^a errors = 95% confidence intervals; ^b direct photolysis in the photo reactor taken into account

The small range of the determined reaction rate constants reflects the relative non-selectivity of $\cdot\text{OH}$ towards organic molecules in aqueous solutions. The rather high uncertainty of the reaction rate constants of 2,6-nonadienal and 1-penten-3-one can be explained with the error

propagation from taking into account direct photolysis. In the case of BHT, the addition of a co-solvent and a mediocre analytical performance did not allow better results. The experiments with the other compounds showed excellent linearity and reproducibility. Furthermore, there is a good agreement between the results from the photoreactor and the γ -radiolysis (Table 4-2).

4.3.2 Ozone

Ozone is often used in drinking water treatment for disinfection and oxidation of micropollutants. It is a highly selective oxidant and reacts predominantly with electron-rich moieties such as olefins, activated aromatic systems, amines and sulfides. A comprehensive description of the ozonation of drinking water is given in [18, 19]. The determined rate constants for the reaction of ozone with the selected T&O compounds are summarized in Table 4-3.

TABLE 4-3. Second order rate constants for the reaction of ozone with selected T&O compounds

Compound	k ($M^{-1}s^{-1}$)	σ ($M^{-1}s^{-1}$) ^a
β -cyclocitral	3890	140
geosmin	0.10	0.03
3-hexen-1-ol	5.4×10^5	0.5×10^5
β -ionone	1.6×10^5	0.1×10^5
2-isopropyl-3-methoxypyrazine	50.2	3.0
2-methylisoborneol	0.35	0.06
2,6-nonadienal	8.7×10^5	0.4×10^5
1-penten-3-one	5.9×10^4	0.1×10^4
BHT	7.4×10^4	0.2×10^4
2,4,6-tribromoanisole	0.020	0.01
2,4,6-trichloroanisole	0.057	0.01

^a errors = 95% confidence intervals

Table 4-3 shows a high reactivity of ozone with compounds containing double bonds (cis-3-hexen-1-ol, 1-penten-3-one, 2,6-nonadienal and β -ionone). In contrast, geosmin und 2-methylisoborneol – both of which are saturated aliphatic compounds – react very slowly with ozone. Even lower is the reactivity of the two investigated anisoles (2,4,6-trichloroanisole and

2,4,6-tribromoanisole). The electron-withdrawing effect of the halogen substituents decreases the reactivity of these compounds substantially ($k_{O_3, \text{anisole}} = 290 \text{ M}^{-1}\text{s}^{-1}$ [20]). The opposite effect could be observed for BHT. The approximately 50-fold increase in reactivity compared to phenol ($k_{O_3, \text{phenol}} = 1300 \text{ M}^{-1}\text{s}^{-1}$ [20]) is due to the alkyl groups, which enhance the reactivity of the aromatic ring.

4.3.3 Ozonation of natural waters

The degradation of compounds during ozonation involves reactions with both ozone and hydroxyl radicals and can be expressed according to eq 3.

$$\ln\left(\frac{[P]}{[P]_0}\right) = -k_{O_3} \int [O_3] dt - k_{OH} \int [OH] dt \quad (3)$$

Using the R_{ct} concept [17], the fraction reacting with ozone is expressed as :

$$f_{O_3} = \frac{k_{O_3}}{k_{O_3} + k_{OH} R_{ct}} \quad (4)$$

$$\text{with: } R_{ct} = \int [OH] dt / \int [O_3] dt \quad (5)$$

The water matrix can have a substantial influence on the stability of ozone and therefore on the ozonation efficiency [18]. This is of particular importance for waters with a high content of natural organic matter (NOM). NOM acts as a promotor for ozone transformation into OH radicals and as a competitor to micropollutants in the reaction with ozone and hydroxyl radicals. It often dominates the oxidation because it is present in the water at much higher concentrations (mg L^{-1} -level) than the target compounds (ng L^{-1} - $\mu\text{g L}^{-1}$).

Fast reacting compounds ($k > 4000 \text{ M}^{-1}\text{s}^{-1}$)

Figure 4-1 shows the effect of NOM on the ozonation efficiency. Although ozone was added at over-stoichiometric levels in all experiments, a complete oxidation of the compounds could be observed only when ozone was present in significant excess. Accordingly, less ozone is needed in Lake Zurich water ($\text{DOC} = 1.2 \text{ mg L}^{-1}$) to achieve the same removal efficiency as in Lake Greifensee water ($\text{DOC} = 3.7 \text{ mg L}^{-1}$). Also, the reactivity of the compounds toward

ozone determines the degree of oxidation which can be achieved in presence of NOM. Hence, a smaller ozone dose is needed to oxidize the fast reacting 2,6-nonadienal compared to the slower reacting 1-penten-3-one and β -cyclocitral.

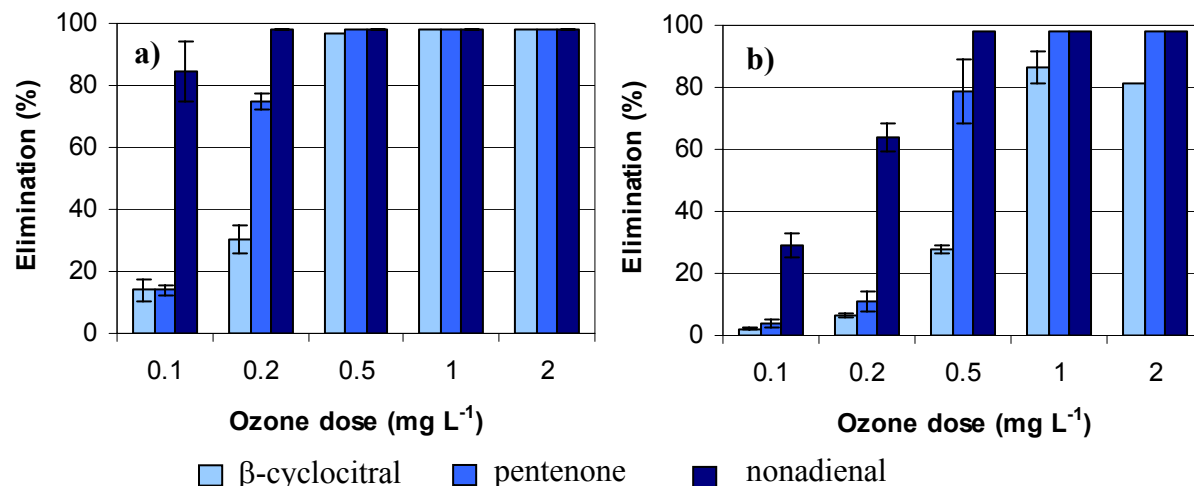


Figure 4-1. Oxidation of fast reacting T&O compounds (initial concentration 0.5 μ M) during ozonation of natural waters at 20-25°C. a) Lake Zurich water (pH 7.9, DOC 1.2 mg L⁻¹, alkalinity 2.6 mM); b) Lake Greifensee water (pH 8.1, DOC 3.7 mg L⁻¹, alkalinity 3.9 mM)

Slow reacting compounds ($k < 4000 \text{ M}^{-1}\text{s}^{-1}$)

Figure 4-2 illustrates the predicted and measured decrease in the concentration of 2-methylisoborneol during ozonation of Lake Zurich water. A similar behaviour could be observed for other compounds and the Lake Greifensee water matrix (data not shown).

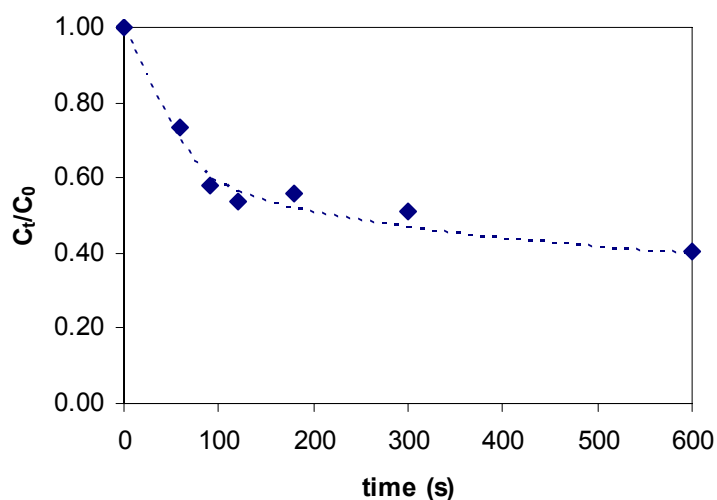


Figure 4-2. Oxidation of 2-methylisoborneol during ozonation of natural water (Lake Zurich). Symbols represent measured concentrations, the line calculated oxidation using eq 3. Conditions: ozone dose = 1 mg L⁻¹, T = 22°C, pH = 7.9

Figure 4-2 shows a fast initial decrease of MIB due to a high $\cdot\text{OH}$ exposure. During the initial phase, ozone is decomposed rapidly and as a consequence the $\cdot\text{OH}$ concentration is high. The determined R_{ct} -values after 30 seconds range between 10^{-7} and 2×10^{-7} . After one minute reaction time the degradation slows down as the exposure with ozone and $\cdot\text{OH}$ levels off. Ozone half-life was approximately one minute in Lake Greifensee water and three minutes in Lake Zurich water. The resulting R_{ct} -values after 15 minutes at the end of the experiment amounted to 5×10^{-8} .

Figure 4-2 also shows that the oxidation of MIB during ozonation can be modelled very well (line) if k_{O_3} and $k_{\cdot\text{OH}}$ are known and the exposures to ozone and $\cdot\text{OH}$ have been determined. by the indigo method and by the decrease of pCBA, respectively. Similar results were obtained for the other slow reacting compounds (data not shown).

Efficiency of ozonation to oxidize the selected T&O compounds

Table 4-4 summarizes the measured and predicted oxidation of T&O compounds during ozonation of natural waters. The calculation of the predicted oxidation is based on eqs 3-5. These results have been obtained with the measured ozone and $\cdot\text{OH}$ exposure in Lake Zurich and Lake Greifensee water for ozone doses of 1 and 2 mg L^{-1} , respectively.

The data in Table 4-4 reveal that with the data set of accurate second order rate constants the oxidation efficiency can be predicted very well once the exposure to ozone and hydroxyl radicals has been determined for a specific water matrix. Furthermore, Table 4-4 clearly shows that ozonation is a powerful technique to mitigate T&O problems. This is also true for compounds which show a low reactivity toward ozone. Ozone is the only relevant oxidant for compounds with $k_{\text{ozone}} > 4000 \text{ M}^{-1}\text{s}^{-1}$. In contrast, geosmin, 2-methylisoborneol and other compounds which react very slowly with ozone are oxidized almost exclusively by hydroxyl radicals. Accordingly, the different degree to which these compounds are oxidized can be attributed to their different reactivity toward hydroxyl radicals. Unexpectedly, the observed oxidation of geosmin was lower than the one of MIB although geosmin exhibits a higher $k_{\cdot\text{OH}}$. This can be explained with the hydroxyl radical exposure, which was considerably lower in the experiment with geosmin than for the other compounds. The high concentration of geosmin spiked to the water matrix might have influenced the $\cdot\text{OH}$ exposure. Under the $\cdot\text{OH}$ exposure that was observed for the other compounds the oxidation efficiency toward geosmin is estimated to amount to 86% for Lake Greifensee water and 79% for Lake Zurich water.

TABLE 4-4. Predicted and measured relative oxidation of T&O compounds (%) during ozonation of natural waters and fraction of the T&O compounds reacting with ozone^a

compound	Lake Zurich water			Lake Greifensee water		
	measured	predicted	f _{ozone}	measured	predicted	f _{ozone}
β-cyclocitral	>98%	100%	91.3%	>98%	100%	89.4%
geosmin	35% ^b	79% ^a 46% ^b	0.03%	50% ^b	86% ^a 64% ^b	0.02%
3-hexen-1-ol	nd ^c	100%	99.9%	nd ^c	100%	99.9%
β-ionone	nd ^c	100%	99.8%	nd ^c	100%	99.7%
2-isopropyl-3-methoxypyrazine	76%	69%	17.0%	78%	76%	14.1%
2-methylisoborneol	59%	64%	0.1%	72%	72%	0.1%
2,6-nonadienal	>98%	100%	99.9%	>98%	100%	99.9%
1-penten-3-one	>98%	100%	99.6%	>98%	100%	99.5%
BHT	nd ^c	100%	99.8%	nd ^c	100%	99.7%
2,4,6-tribromoanisole	60%	53%	0.01%	64%	61%	0.01%
2,4,6-trichloroanisole	nd ^c	64%	0.02%	nd ^c	72%	0.02%

^a conditions: ozone dose = 1 mg L⁻¹ for Lake Zurich water and 2 mg L⁻¹ for Lake Greifensee water, contact time = 10 min, T = 20-25°C; ozone exposure = 4 × 10⁻³ Ms, [•]OH exposure = 2 × 10⁻¹⁰ Ms for Lake Zurich water and 2.5 × 10⁻¹⁰ Ms for Lake Greifensee water

^b conditions: same as above^a, except [•]OH exposure = 0.8 × 10⁻¹⁰ Ms for Lake Zurich water and 1.3 × 10⁻¹⁰ Ms for Lake Greifensee water

^c nd = not determined

If the oxidation of compounds during ozonation is not satisfactory, it can be substantially accelerated by increasing the [•]OH exposure, which results in higher R_{ct}-values. To achieve this goal, several options generally referred to as advanced oxidation processes (AOPs) are possible. One possibility is the combination of ozone with hydrogen peroxide (H₂O₂) to achieve a faster decomposition of ozone into [•]OH [18]. Although ozone based AOPs have been shown to be promising in oxidizing ozone-resistant compounds [12], special attention has to be paid to bromate formation. This requires higher overall oxidant dosages, which in turn enhances bromate formation. Bromate is formed during ozonation of bromide-containing waters [21, 22] and has been classified as potential human carcinogen with a drinking water standard of 10 µg/L. Experiments in natural waters showed that a better oxidation efficiency of MTBE (methyl *tert*-butyl ether) in an O₃/H₂O₂ based process was achieved if the ozone dose was increased substantially from 2 mg/L to 4 mg/L [23]. Under these conditions,

however, the drinking water standard of bromate was exceeded for two of the three investigated waters containing 50 µg/L bromide because of the higher overall oxidant exposure. In the case of geosmin and 2-methylisoborneol a better selectivity, i.e. oxidation vs bromate formation, can be expected because their second order rate constants for the reaction with $\cdot\text{OH}$ are significantly higher than for MTBE ($k_{\text{MTBE}, \cdot\text{OH}} = 1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [23]).

In general, ozonation of T&O compounds can be optimized when accurate second order rate constants are available with special attention to bromate formation. If this is not possible, the AOP UV/H₂O₂ could be considered because no bromate is formed in this process [22].

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Chapter 5

Oxidation of T&O compounds and bromate formation

Investigation of conventional ozonation and advanced oxidation
processes (AOPs) in laboratory- and pilot-scale

Abstract

The applicability of conventional ozonation and ozone-based advanced oxidation processes (AOPs) to mitigate taste and odor problems in drinking water was investigated. The experiments were performed with natural water (Lake Zurich) in laboratory- and pilot-scale. The study showed that the T&O removal efficiency of ozonation for a contact time of 10-20 min could be improved by applying AOPs based on ozone/hydrogen peroxide. The reaction time to achieve a certain removal of T&O compounds with low to moderate reactivity toward ozone ($k_{\text{ozone}} < \sim 500 \text{ M}^{-1}\text{s}^{-1}$) was approximately one order of magnitude shorter in the AOP $\text{O}_3/\text{H}_2\text{O}_2$ than in conventional ozonation for a given ozone dose. Additionally, the AOP $\text{O}_3/\text{H}_2\text{O}_2$ resulted in a lower formation of the potentially carcinogenic bromate, an oxidation by-product formed during ozonation of bromide-containing waters. This study showed that results obtained in laboratory-scale experiments could be up-scaled successfully to a $5.6 \text{ m}^3/\text{h}$ pilot plant.

5.1 Introduction

Most of the taste and odor (T&O) problems in drinking water do not occur throughout the year, but are limited to a few weeks with peak concentrations. This is especially true for surface water related T&O compounds because these compounds are often strongly linked to the seasonal occurrence of phytoplankton species (Chapter 3). Hence, water utilities which distribute surface water must be able to quickly adapt to these T&O events to mitigate the public impact of bad taste in the drinking water. Towards this end, flexible drinking water treatment processes are required which allow a fast adjustment to T&O episodes. Such measures should be possible without causing disproportional operational costs.

In Chapter 4, the potential of ozonation for T&O removal during drinking water treatment was discussed. An oxidation of typical T&O compounds by more than 50% was observed under common drinking water ozonation conditions. Hence, it was concluded that ozonation was a powerful technique to mitigate T&O problems even for compounds with low reactivity toward ozone. These compounds, such as the potent T&O compounds geosmin and 2-methylisoborneol, are oxidized almost exclusively by hydroxyl radicals ($\cdot\text{OH}$), which are formed during the decomposition of ozone (Chapter 4). However, a 50% reduction during ozonation might not be sufficient to decrease the concentration of potent T&O compounds below their respective odor thresholds. As discussed in the previous chapter, enhanced oxidation can be achieved with an increased ozone dose. However, higher ozone doses are likely to cause problems with high ozone residuals at the outlet of the reactor and oxidation by-products, such as AOC (assimilable organic carbon) and the potentially carcinogenic bromate (drinking water standard in Switzerland, E.U. and U.S.: $10\text{ }\mu\text{g L}^{-1}$). Bromate is formed in a complex system with parallel ozone and $\cdot\text{OH}$ reactions during ozonation of bromide-containing waters [1, 2]. A simplified scheme of the bromate formation mechanism is given in Figure 5-1.

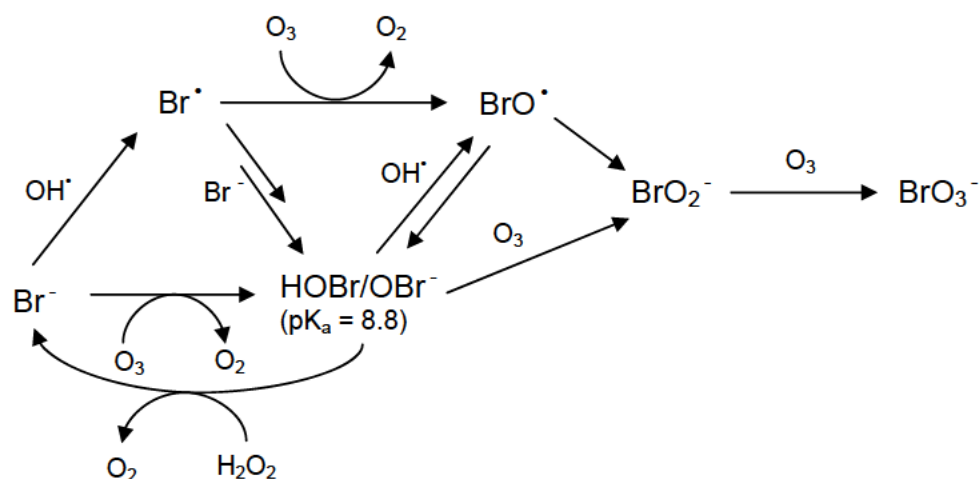


Figure 5-1: Bromate (BrO_3^-) formation during ozone-based oxidation processes (adapted from [3, 4]).

As concluded in the previous chapter, advanced oxidation processes (AOPs) could be an interesting alternative to conventional ozonation for ozone-resistant compounds. Several ozone-based AOPs have been described in the literature [5], e.g., (i) in combination with hydrogen peroxide ($\text{O}_3/\text{H}_2\text{O}_2$), (ii) irradiation with UV-light (O_3/UV), (iii) increase of pH or (iv) contact with activated carbon (carbazone process [6, 7]). AOPs offer the advantage of an accelerated removal of these compounds because they stimulate the decomposition of ozone through the radical chain to $\cdot\text{OH}$ [5]. Whereas the full oxidation capacity of ozone is often not exhausted in real reactor systems, ozone is rapidly depleted in AOPs. Hence, in reactors that function as AOPs higher Rct-values (ratio of $\cdot\text{OH}$ -exposure to ozone exposure [8]) can be achieved than in conventional ozonation processes. This effect is especially pronounced for waters which are low in DOC (dissolved organic carbon), such as groundwaters. Surface waters with high DOC levels exhibit similar ozone exposures and ozone transformation rates as AOPs because of the very fast ozone depletion. Generally, a decrease in ozone exposure is the equivalent of a decreased disinfection efficiency. Therefore, the implementation of an AOP has to be carefully adjusted to site-specific requirements with regard to disinfection, oxidation and by-product formation. As for bromate formation, a general statement whether the implementation of an ozone-based AOP leads to less bromate can not be made because of the complexity of the involved parallel ozone and $\cdot\text{OH}$ reactions. However, in an AOP with hydrogen peroxide (H_2O_2) less bromate formation can be expected because H_2O_2 reacts with

the intermediate HOBr/OBr^- back to bromide (Fig. 5-1 and refs. [2, 4]). In contrast to ozone-based AOPs, no bromate is formed in the AOP $\text{UV}/\text{H}_2\text{O}_2$ [2].

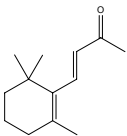
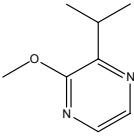
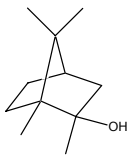
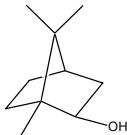
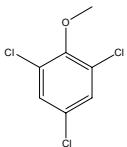
Because the AOP $\text{O}_3/\text{H}_2\text{O}_2$ can easily be implemented into an existing ozone reactor and exhibits low operating costs, this process was selected for further investigation in this study. In this chapter, the AOP $\text{O}_3/\text{H}_2\text{O}_2$ is compared with conventional ozonation with respect to T&O removal and bromate formation both for bench-scale and pilot-scale. Lake water from Lake Zurich ($\text{DOC } 1.4 \text{ mg L}^{-1}$) which was spiked with very low amounts of T&O compounds ($0.01 \text{ }\mu\text{M}$) was used for the experiments in order to mimic natural conditions. Additionally, the lake water was spiked with various bromide levels to investigate the applicability of ozonation for T&O control in waters with elevated bromide levels.

5.2 Materials and Methods

5.2.1 Standards and reagents

Four T&O compounds, whose reaction rate constants toward ozone and $\cdot\text{OH}$ were determined previously (Chapter 4), were selected for this study. The selected compounds covered a wide range of ozone reactivity. Table 5-1 summarizes the kinetic data of the four compounds.

TABLE 5-1. Investigated T&O compounds

compound	structure	$k_{\text{O}_3} [\text{M}^{-1}\text{s}^{-1}]^a$	$k_{\text{OH}} [10^9 \text{M}^{-1}\text{s}^{-1}]^a$
β -ionone		$1.6 \pm 0.13 \times 10^5$	7.79 ± 0.34
2-isopropyl-3-methoxypyrazine (IPMP)		50 ± 3	4.91 ± 0.13
2-methylisoborneol (MIB) ^b		0.35 ± 0.06	5.09 ± 0.14
isoborneol ^c		n.a. ^d	n.a. ^d
2,4,6-trichloroanisole (TCA) ^b		0.06 ± 0.01	5.10 ± 0.11

^a rate constants determined at 20 – 25°C (Chapter 4) ; errors = 95% confidence intervals

^b only in lab-scale experiments

^c only in pilot-scale experiments (proxy for MIB and TCA)

^d n.a. = not available (expected to be similar as the reaction rate constants for MIB)

Ozone was produced with a CMG 3-3 ozone generator (Apaco AG, Grellingen, Switzerland) as described in the previous chapter. The experiments were performed in Lake Zurich water, which was taken at a depth of 30 m (pH 7.9; DOC 1.4 mg L⁻¹; alkalinity 2.5 mM). The water for the laboratory experiments was filtered immediately upon arrival (0.45 μm cellulose nitrate filters) and stored in the dark at 4°C. The water for the pilot plant study was pumped

directly from the lake into the ozone reactor with a preceding pre-filtration (micro-filtration). The different filtration in the laboratory- and pilot-scale experiments is not expected to have significantly influenced the outcome of the experiments because the stability of ozone and $\cdot\text{OH}$ is mainly governed by dissolved organic material, which is not retained in the applied filtration steps.

5.2.2 Analytical methods

Below, a short description of the applied analytical methods is given. Detailed information on the determination of the ozone and $\cdot\text{OH}$ exposure can be found in Chapter 4.

Ozone. Dissolved ozone was analyzed with the Indigo method [9].

Hydroxyl radicals / pCBA. The $\cdot\text{OH}$ exposure was determined with pCBA (4-chlorobenzoic acid, $k_{\cdot\text{OH}} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) with a negligible reactivity towards ozone ($k_{\text{O}_3} < 0.15 \text{ M}^{-1}\text{s}^{-1}$ [10]). pCBA was analysed with HPLC-UV (Agilent 1100 series) at 234 nm (injection: 100 μL ; flow: 1 mL min^{-1} ; eluent: 60% MeOH / 40% H_3PO_4 50 mM; column: CC125/4 Nucleosil 100-5 C18 (Macherey Nagel, Oensingen, Switzerland)).

T&O compounds. The low T&O concentrations ($< 0.01 \mu\text{M}$) required a highly sensitive method for their analysis. In this study, GC-MS (GC 8000 coupled to a Quadrupole-MS (MD800; Fisons Instruments) with the MS in the single ion mode (SIM)) combined with headspace-SPME (solid phase micro extraction) was applied. A detailed description of this method and the parameters for the quantitative analysis of the investigated T&O compounds can be found in Chapter 2. The detection limits for the investigated compounds were between 0.5 and 1 ng L^{-1} (approximately $5 \times 10^{-12} \text{ M}$). The standard error of the method within the concentration range that was investigated in these experiments ($10^{-9} - 10^{-7} \text{ M}$) was between 1 and 10%.

Hydrogen peroxide. In the laboratory-scale experiments, the H_2O_2 -concentration of the stock solution was determined photometrically at 240 nm ($\epsilon = 40 \text{ M}^{-1} \text{ cm}^{-1}$). In the pilot-scale experiments, the H_2O_2 -concentration was determined in order to control the performance of the dosing pump (see below) and to verify whether there was no residual H_2O_2 after ozonation. Towards this end, the concentration of H_2O_2 was determined with a DPD-based method [11]. The principle of the method is the oxidation of DPD (N,N-diethyl-p-

phenylendiamine) in the presence of H_2O_2 and a catalyst (peroxidase) to the radical cation DPD^{+} . This cation can be measured spectro-photometrically ($\epsilon_{551\text{nm}} = 21'000 \text{ M}^{-1}\text{cm}^{-1}$).

Bromide and bromate. These two ions were measured with ion-chromatography. The applied method is based on an ion chromatography followed by a sequential analysis through conductivity (bromide) and sub-sequent post-column reaction with UV detection (bromate) [12]. The quantification limit was $5 \mu\text{g L}^{-1}$ for bromide and $1 \mu\text{g L}^{-1}$ for bromate. The standard error of the method was 10% and 20% near the quantification limit, respectively.

5.2.3 Experiments

Experiments were performed in laboratory batch systems and on a pilot plant of the water utility of Zurich. The aim of the laboratory-scale experiments was to gain time-resolved information with a set of different initial concentrations of bromide and ozone. The principle of the pilot plant experiments was similar, but instead of the kinetics, stationary conditions with contact times between 4 and 20 min were investigated in the ozone reactor. Table 5-2 gives an overview of the initial conditions that were investigated in all possible combinations in this study.

TABLE 5-2. Initial conditions of the ozonation experiments in laboratory- and pilot-scale

Compound	Laboratory-scale	Pilot-scale
T&O compounds ^a	0.01 μM	0.01 μM
pCBA	0.5 – 1 μM	1.5 μM
Bromide	20; 80; 130 $\mu\text{g L}^{-1}$ ^b	20 and 80 $\mu\text{g L}^{-1}$ ^b
Ozone	1; 2; 5 mg L^{-1} (21; 42; 104 μM)	0.8 and 2.5 mg L^{-1} (17 and 52 μM)
H_2O_2	10; 20; 50 μM ^c	10 and 30 μM ^c

^a laboratory-scale: β -ionone, IPMP, MIB and TCA; pilot-scale: β -ionone, IPMP and isoborneol
^b natural background of Lake Zurich approximately 20 $\mu\text{g L}^{-1}$
^c only in the AOP $\text{O}_3/\text{H}_2\text{O}_2$ experiments; approximately half-stoichiometric addition of H_2O_2 to initial ozone dose

Laboratory-scale experiments

Bench-scale experiments were performed as duplicates at room temperature (20-25°C). Filtered water from Lake Zurich was buffered to pH 8 with 5 mM borate and spiked with each of the four T&O compounds at 0.01 μM , with pCBA at 0.5 - 1 μM and different levels of bromide. The experiments were performed in 250 mL bottles, which were equipped with a dispenser unit to enable reproducible sample amounts at specified time intervals. Ozone stock solution was added to the reactor solution with a glass syringe to reach the desired initial concentration. In the AOP experiments, hydrogen peroxide was added at half-stoichiometric concentrations relative to ozone prior to the ozone injection. Additionally, a sample was withdrawn before ozone addition to check for a potential oxidation of the spiked compounds by H_2O_2 .

Pilot-scale experiments

These experiments were performed at the ozone reactor of a pilot plant, consisting of ozonation, activated carbon filtration and ultrafiltration. The ozone reactor is schematically shown in Figure 5-2. It consisted of four chambers with a total volume of 2 m^3 and an average flow of 5.6 $\text{m}^3 \text{h}^{-1}$. Hence, the mean contact time in the ozone reactor was around 20 min. Tracer experiments which were performed with a dye to assess the hydraulic behavior showed that the reactor behaved as a turbulent plug-flow reactor [13]. Ozone was added through a rapid mixer and measured on-line at the inlet of the reactor. This inlet concentration was maintained automatically in case of small fluctuations in the raw water quality. The mean water temperature during the pilot-scale experiments was around 10°C.

Two pumps were installed for a continuous dosing of the reaction solutions. A concentrate of the T&O compounds (7.5 μM), bromide (no additional bromide and 45 mg L^{-1} , respectively) and pCBA (1.12 mM) was dosed with a rate of 7.5 L h^{-1} at the inlet of the reactor to achieve the desired initial concentrations (Table 5-2). For practical reasons, only three T&O compounds were spiked in the pilot-scale experiments (IPMP, isoborneol and β -ionone). Isoborneol and pCBA served as proxies for MIB and TCA because of the comparable reactivity towards ozone and $\cdot\text{OH}$. For the dosing of H_2O_2 , a concentrated solution (14 mM) was pre-mixed with effluent water from the ozone reactor at a rate of 4 L h^{-1} . This H_2O_2 solution was subsequently dosed at a rate of 400 L h^{-1} between sampling points 2 and 3 counter-current to the water flow with a tube that went across the reactor and contained small holes for a homogeneous dosing of the solution (Fig. 5-2). After the ozone dose had been

adjusted to the desired level and the dosing pumps have been turned on, the system was equilibrated for at least one hour. After steady-state conditions had been reached in the reactor, each sampling point was sampled five times.

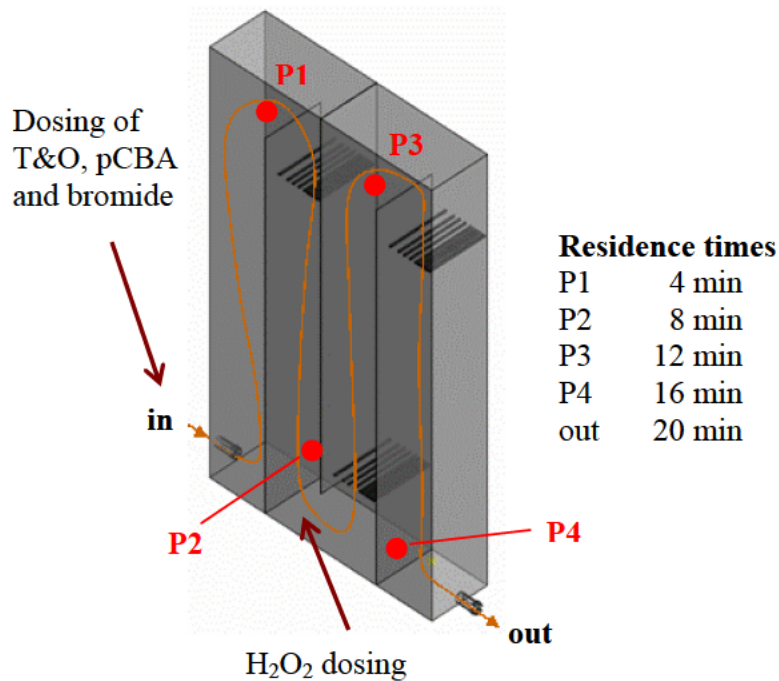


Figure 5-2: Ozone reactor in the pilot plant with sampling points (P1 – P4) and entry points for dosing of reaction solutions (arrows). The orange line indicates the water flow through the reactor. The black bars symbolize obstacles that were installed to create a better flow regime in the reactor.

5.3 Results and Discussion

5.3.1 Laboratory-scale experiments

Ozone and hydroxyl radicals exposures

Figures 5-3 and 5-4 show the ozone and $\cdot\text{OH}$ exposures, i.e., the integrated concentrations of these oxidants over time, that were determined in the laboratory-scale experiments. It can clearly be seen that the ozone exposure was substantially smaller in the AOP ($\text{O}_3/\text{H}_2\text{O}_2$) than in conventional ozonation. The reason behind this finding is the drastically decreased life time of ozone due to the addition of H_2O_2 . In all the AOP experiments, the half-life time of ozone was around 20 s, whereas in conventional ozonation the ozone stability depended to a high degree on the initial ozone concentration (half-life between 130 s for 1 mg L^{-1} ozone and 320 s for 5 mg L^{-1} ozone). As a consequence of the fast ozone decomposition in the AOP $\text{O}_3/\text{H}_2\text{O}_2$, the respective ozone and $\cdot\text{OH}$ exposures leveled off after approximately 100 s. In conventional ozonation, however, there was still residual ozone left after 600 s, which led to constantly increasing exposures of both ozone and $\cdot\text{OH}$ during the experiment. This incomplete ozone transformation in conventional ozonation resulted in lower $\cdot\text{OH}$ exposures after 600 s compared to the corresponding exposures in the AOPs $\text{O}_3/\text{H}_2\text{O}_2$. This is shown in Fig. 5-4 for ozone doses of 2 mg L^{-1} and 5 mg L^{-1} .

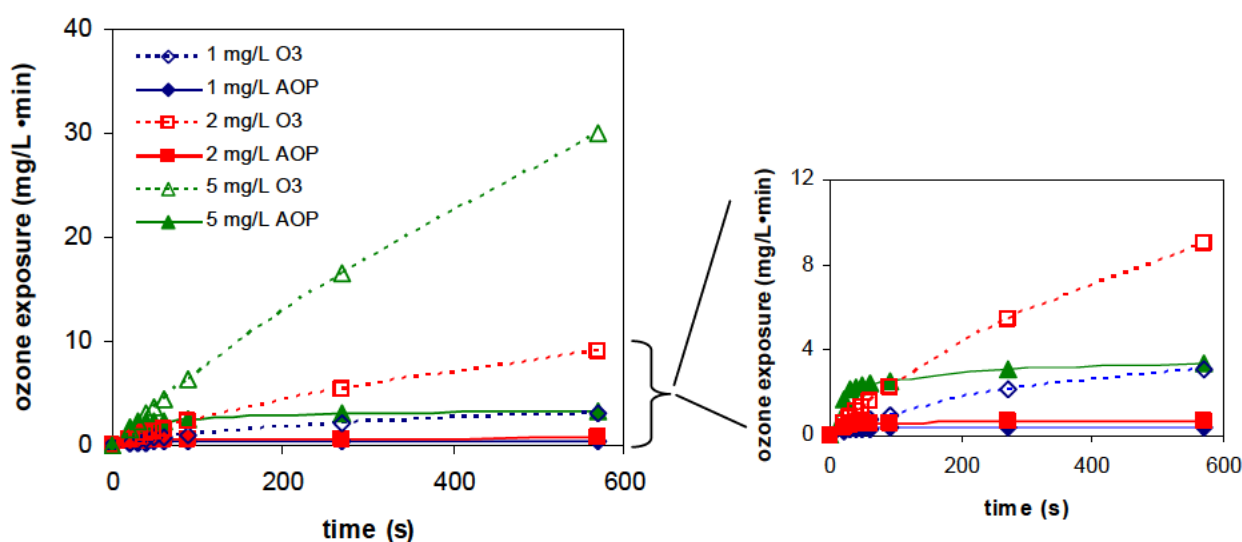


Figure 5-3: Ozone exposures in laboratory-scale experiments. O_3 : conventional ozonation; AOP: $\text{O}_3/\text{H}_2\text{O}_2$. Conditions: Lake Zurich water (pH 8; DOC 1.4 mg L^{-1} ; alkalinity 2.5 mM); room temperature ($20\text{--}25^\circ\text{C}$).

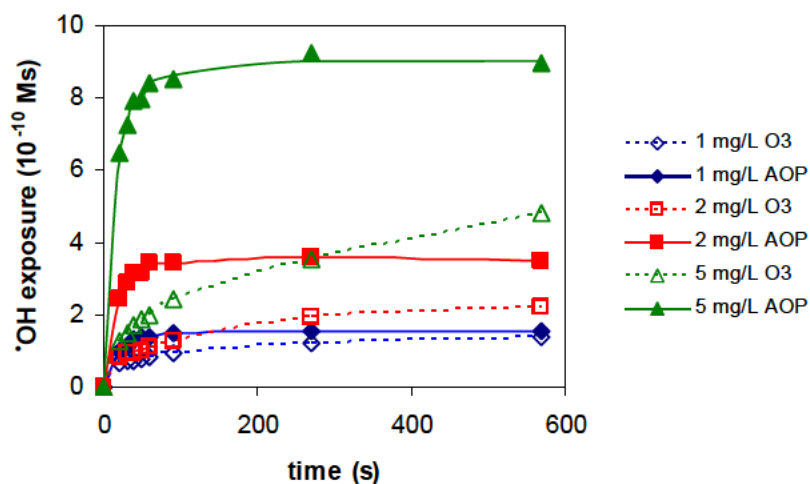


Figure 5-4: Hydroxyl radical exposures in laboratory-scale experiments. O₃: conventional ozonation; AOP: O₃/H₂O₂. Conditions: Lake Zurich water (pH 8; DOC 1.4 mg L⁻¹; alkalinity 2.5 mM); room temperature (20-25°C). The [•]OH exposure is based on the decrease of pCBA (initial concentration: 0.5 - 1 μM).

Removal of T&O compounds

Figure 5-5 shows the degradation of IPMP and TCA during conventional ozonation and the AOP O₃/H₂O₂. The concentration profiles of these two T&O compounds are shown for the corresponding ozone and [•]OH-exposures of Figures 5-3 and 5-4. As IPMP and TCA react slowly with ozone, their degradation was considerably accelerated in the AOP. In the AOP, the reaction was terminated after approximately 100 s due to the complete depletion of ozone. After this time, a similar or even higher oxidation of the T&O compounds had been achieved than during 10 min of conventional ozonation. This is due to incomplete ozone transformation in the conventional ozonation process. Consistently, IPMP showed a slightly higher degradation than TCA in the conventional ozonation process because it has a higher rate constant for the reaction with ozone (Table 5-1 and Fig. 5-6). MIB showed very similar degradation profiles to TCA (data not shown). In contrast, β-ionone, which reacts quickly with ozone, was degraded to more than 99% after 20s in all experiments (data not shown).

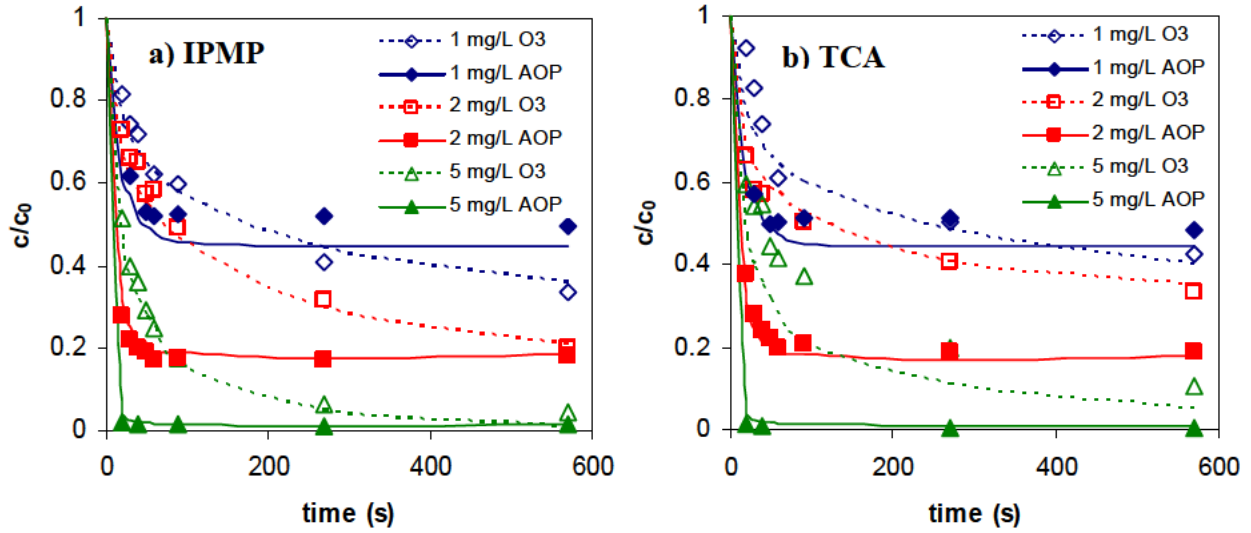


Figure 5-5: Transformation of IPMP (a) and TCA (b) in laboratory-scale experiments. Symbols represent measured concentrations, the lines calculated oxidation using eq 1. O₃: conventional ozonation; AOP: O₃/H₂O₂. Conditions: Lake Zurich water (pH 8; DOC 1.4 mg L⁻¹; alkalinity 2.5 mM); room temperature (20-25°C); ozone doses: 1, 2, 5 mg L⁻¹; O₃:H₂O₂ ratio: 1:0.5 (M:M). Initial concentrations: IPMP = 0.01 μM (1.5 μg L⁻¹); TCA = 0.01 μM (2.1 μg L⁻¹).

As introduced in Chapter 4, the degradation of compounds during ozonation can be calculated according to eq 1 by using the second order rate constants for the reaction with ozone and [•]OH (Table 5-1) and the corresponding ozone and [•]OH exposures ($\int [O_3]dt$ and $\int [^{\bullet}OH]dt$). With this calculation, the removal of the investigated T&O compounds could be predicted accurately in all laboratory experiments (Fig. 5-5).

$$\ln\left(\frac{[P]}{[P]_0}\right) = -k_{O_3} \int [O_3]dt - k_{OH} \int [^{\bullet}OH]dt \quad (1)$$

The fraction reacting with ozone (f_{O_3}) can be expressed as:

$$f_{O_3} = \frac{k_{O_3} \int [O_3]dt}{k_{O_3} \int [O_3]dt + k_{OH} \int [^{\bullet}OH]dt} \quad (2)$$

Using the R_{ct} concept [8], eq 2 can be expressed as:

$$f_{O_3} = \frac{k_{O_3}}{k_{O_3} + k_{OH}R_{ct}} \quad (3)$$

$$\text{with: } R_{ct} = \int [^{\bullet}OH]dt / \int [O_3]dt \quad (4)$$

The R_{ct} -values obtained in the laboratory-scale experiments for the initial 10 min were $1.3 \times 10^{-8} - 4 \times 10^{-8}$ for conventional ozonation and $3 \times 10^{-7} - 5 \times 10^{-7}$ for the AOP O_3/H_2O_2 (Fig. 5-6). The higher R_{ct} -values in the AOP O_3/H_2O_2 indicate the faster transformation of ozone to $\cdot OH$.

Figure 5-6 illustrates the role of ozone and $\cdot OH$ in the degradation of the investigated T&O compounds. Evidently, β -ionone reacted to more than 90% with ozone even in the AOP O_3/H_2O_2 , where ozone was rapidly decomposed. As for IPMP, the reaction with ozone contributed to a substantial degree (approximately 40%) to the overall degradation in conventional ozonation, but was negligible in the AOP O_3/H_2O_2 . In contrast, hydroxyl radicals were the only relevant oxidants for the removal of TCA and MIB. Therefore, AOPs are most appropriate if compounds with low reactivity towards ozone have to be oxidized.

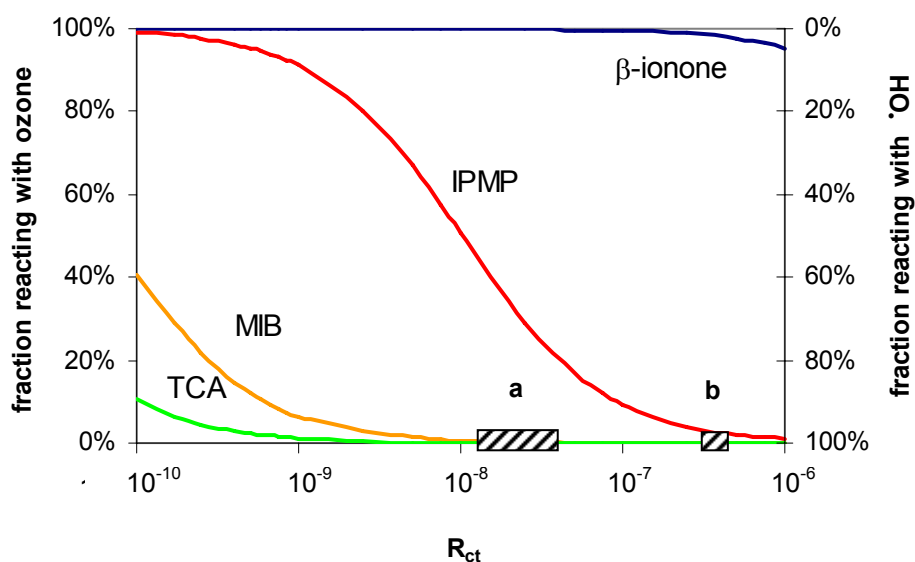


Figure 5-6: Fraction of the T&O compounds reacting with ozone and $\cdot OH$ with respect to the R_{ct} -value (eq 4). a and b: R_{ct} -values for the initial 10 min of reaction (a: conventional ozonation; b: AOP O_3/H_2O_2).

Bromate formation

Bromate formation was investigated in Lake Zurich water with initial bromide concentrations of 20, 80 and $130 \mu g L^{-1}$ for conventional ozonation and the AOP O_3/H_2O_2 . In Figure 5-7, the kinetics of bromate formation in spiked Lake Zurich water ($80 \mu g L^{-1}$ bromide) are shown for conventional ozonation and the AOP O_3/H_2O_2 . The reaction was completed after about 100s in the AOP due to the full depletion of ozone. Conventional ozonation experiments ended up with considerably higher bromate levels because of the higher ozone exposures and the

absence of H_2O_2 . H_2O_2 reacts with the reaction intermediate HOBr/OBr^- and leads to a reduced bromate formation (Fig. 5-1). Nevertheless, the kinetics of bromate formation were comparable to the AOP $\text{O}_3/\text{H}_2\text{O}_2$ in the first 100s.

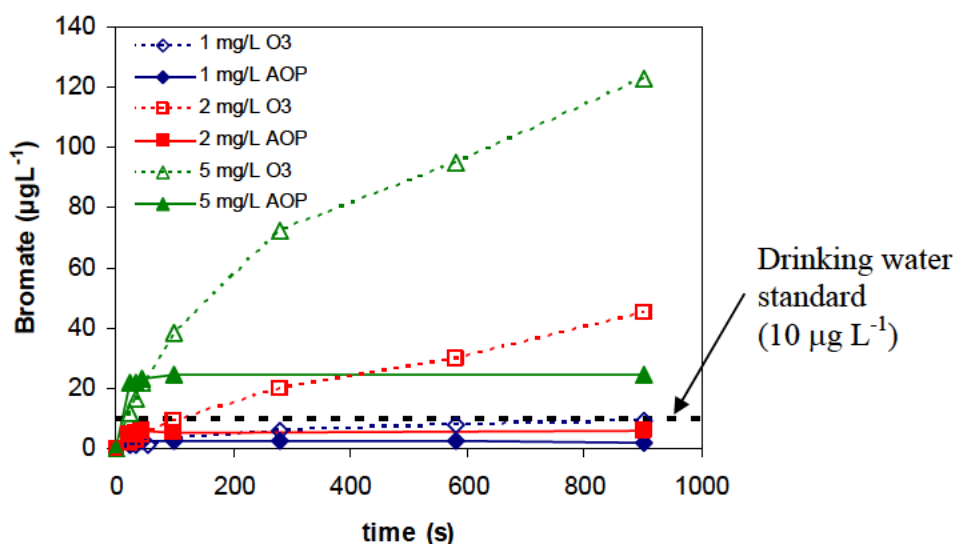


Figure 5-7: Bromate formation in laboratory-scale experiments. O_3 : conventional ozonation; AOP: $\text{O}_3/\text{H}_2\text{O}_2$. Conditions: spiked Lake Zurich water (pH 8; DOC 1.4 mg L^{-1} ; alkalinity 2.5 mM ; bromide level 80 µg L^{-1}); room temperature ($20\text{--}25^\circ\text{C}$); ozone doses: 1, 2, 5 mg L^{-1} ; $\text{O}_3:\text{H}_2\text{O}_2$ ratio: 1:0.5 (M:M).

In Table 5-3, the bromate endpoints after complete ozone decomposition are summarized for conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$.

TABLE 5-3. Bromate formation in Lake Zurich water with variable initial bromide concentrations (laboratory-scale experiments).

Initial bromide (µg L^{-1})	ozone dose in conventional ozonation			ozone dose in AOP $\text{O}_3/\text{H}_2\text{O}_2$ ($\text{O}_3:\text{H}_2\text{O}_2$ ratio: 1:0.5 (M:M))		
	1 mg L^{-1}	2 mg L^{-1}	5 mg L^{-1}	1 mg L^{-1}	2 mg L^{-1}	5 mg L^{-1}
bromate endpoints after complete ozone decomposition (in µg L^{-1})						
20	<1	5.9	20.0	<1	1.3	6.1
80	9.3	44.8	122.9	1.0	6.2	24.6
130	9.2	75.0	179.0	2.3	15.0	55.0

Obviously, conventional ozonation is only suitable with respect to bromate formation in case of low bromide levels and low ozone doses. Already with an ozone dose of 2 mg L^{-1} , the drinking water standard for bromate (10 µg L^{-1}) was prominently exceeded in waters with elevated bromide levels. However, bromate formation could be considerably reduced by addition of hydrogen peroxide. This can be explained by the decreased ozone exposure and

the reduction of the intermediate HOBr to bromide by H_2O_2 (Fig. 5-1). Despite a considerable reduction in bromate formation, exceeding bromate levels can not be avoided by the addition of H_2O_2 in extreme cases of very high ozone doses and bromide levels.

Bromate formation and T&O removal for complete ozone depletion are shown for Lake Zurich water in Figure 5-8. The data reveal that an 80% reduction of the investigated T&O compounds can be achieved with an ozone dose of 2 mg L^{-1} . If this T&O reduction is sufficient, conventional ozonation can be applied in waters with low bromide levels without creating bromate problems. However, if all T&O compounds are to be degraded by more than 80%, conventional ozonation is likely to create bromate problems even in waters with a relatively low bromide level. In Lake Zurich water with a bromide level of approximately $20 \mu\text{g L}^{-1}$, an ozone dose of 5 mg L^{-1} resulted in bromate concentrations above the drinking water standard of $10 \mu\text{g L}^{-1}$. In cases where high ozone doses have to be applied to mitigate T&O problems, the advantage of AOPs becomes evident. This study revealed that a faster and often slightly enhanced absolute oxidation of T&O compounds can be achieved (Fig. 5-5) with significantly less bromate formation. Figure 5-8 shows that in the case of Lake Zurich water, an ozone dose of 5 mg L^{-1} could be applied without exceeding the drinking water standard for bromate.

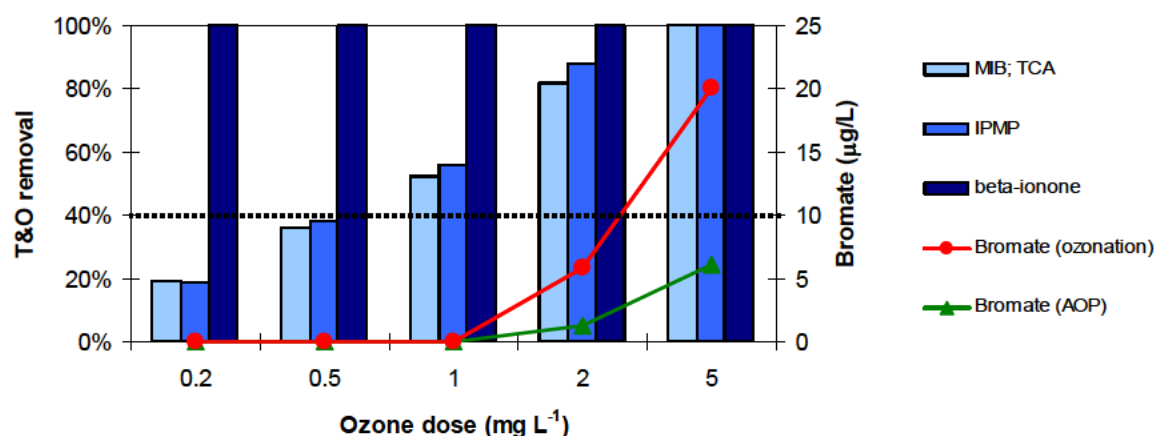


Figure 5-8: Removal of T&O compounds and bromate formation during ozonation of Lake Zurich water. T&O removal: endpoints after complete ozone decomposition in conventional ozonation (the AOP $\text{O}_3/\text{H}_2\text{O}_2$ gives similar results ($\pm 10\%$) for the same ozone dose). Initial concentrations of T&O compounds: $0.01 \mu\text{M}$ ($1.5 - 2.1 \mu\text{g L}^{-1}$). Bromate formation: endpoints after complete ozone decomposition in conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$. Conditions: Lake Zurich water (pH 8; DOC 1.4 mg L^{-1} ; alkalinity 2.5 mM ; bromide level $20 \mu\text{g L}^{-1}$); room temperature ($20-25^\circ\text{C}$). The black dotted line represents the drinking water standard for bromate ($10 \mu\text{g L}^{-1}$).

5.3.2 Pilot-scale experiments

Ozone and hydroxyl radicals exposures

Figure 5-9 shows the exposures of the two oxidants in the ozone reactor of the pilot plant. With an enhanced $\cdot\text{OH}$ -formation and a quick leveling-off of the ozone exposure after H_2O_2 -addition, the relative behavior of the exposures is similar to the bench-scale experiments (Figs. 5-3 and 5-4). Differences in the absolute exposures can be explained with the higher ozone stability in the cold water of the pilot plant (10°C) and the different dosing of H_2O_2 and aqueous ozone. In the pilot plant, H_2O_2 was not dosed at the entrance of the reactor, but in the middle between P2 and P3. With this setting, ozone was available for disinfection in the first half of the reactor and was then completely transformed into $\cdot\text{OH}$ after H_2O_2 addition. The residual H_2O_2 was quickly degraded in the surface layer of the activated carbon filter which followed the ozone reactor (data not shown). In contrast, conventional ozonation showed incomplete ozone transformation in the reactor and consequently, a continuing increase in the ozone exposure. Residual ozone concentrations in conventional ozonation were 0.3 mg L^{-1} for an inlet concentration of 0.8 mg L^{-1} and 1.5 mg L^{-1} for an inlet concentration of 2.5 mg L^{-1} , respectively.

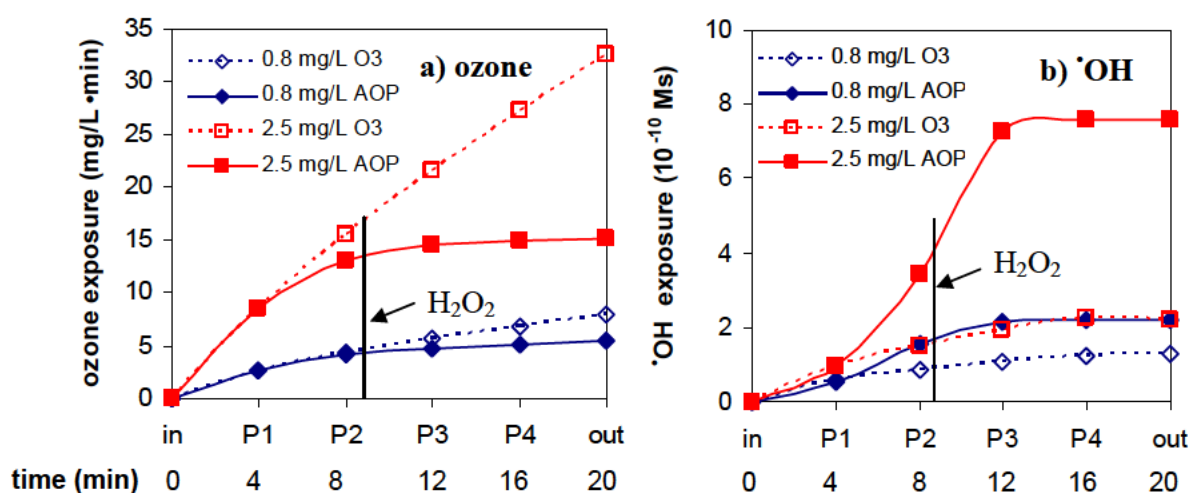


Figure 5-9: Ozone (a) and hydroxyl radicals (b) exposures in pilot-scale experiments. O₃: conventional ozonation; AOP: O₃/H₂O₂. Conditions: Lake Zurich water (pH 7.9; DOC 1.4 mg L^{-1} ; alkalinity 2.5 mM); 10°C . The corresponding residence time had been determined in tracer experiments (Fig. 5-2). The $\cdot\text{OH}$ exposure is based on the decrease of pCBA (initial concentration: $1.5\text{ }\mu\text{M}$).

For a comparison of the laboratory- and pilot-scale experiments, it has to be taken into account that in the pilot ozonation reactor aqueous ozone was added to the water before the dosing point of the T&O compounds and bromide (reactor inlet). Hence, the ozone

concentration which was measured at the inlet did not correspond to the original ozone dose. In contrast, ozone was added after the addition of the T&O compounds and bromide in the bench-scale experiments. The first phase after the addition of ozone is characterized by a fast ozone depletion [5], which - in combination with the higher temperature - led to lower ozone exposures in the laboratory-scale experiments.

Removal of T&O compounds

Figure 5-10 illustrates the removal of T&O compounds in the pilot ozonation reactor. With its comparable reactivity towards ozone and $\cdot\text{OH}$, pCBA served as a surrogate for MIB and TCA, which were not spiked to the water in the pilot plant experiments. β -ionone had already been degraded by more than 99% at sampling point P1 (data not shown). Figure 5-10 also shows a comparison of the pilot-scale and the bench-scale experiments. This comparison reveals that IPMP and pCBA (TCA) showed a similar behavior to the bench-scale experiments (Fig. 5-5): (i) a better removal of IPMP than pCBA (TCA) due to the reactivity with both ozone and $\cdot\text{OH}$ and (ii) an enhanced and accelerated removal of both compounds after the addition of H_2O_2 due to complete ozone transformation.

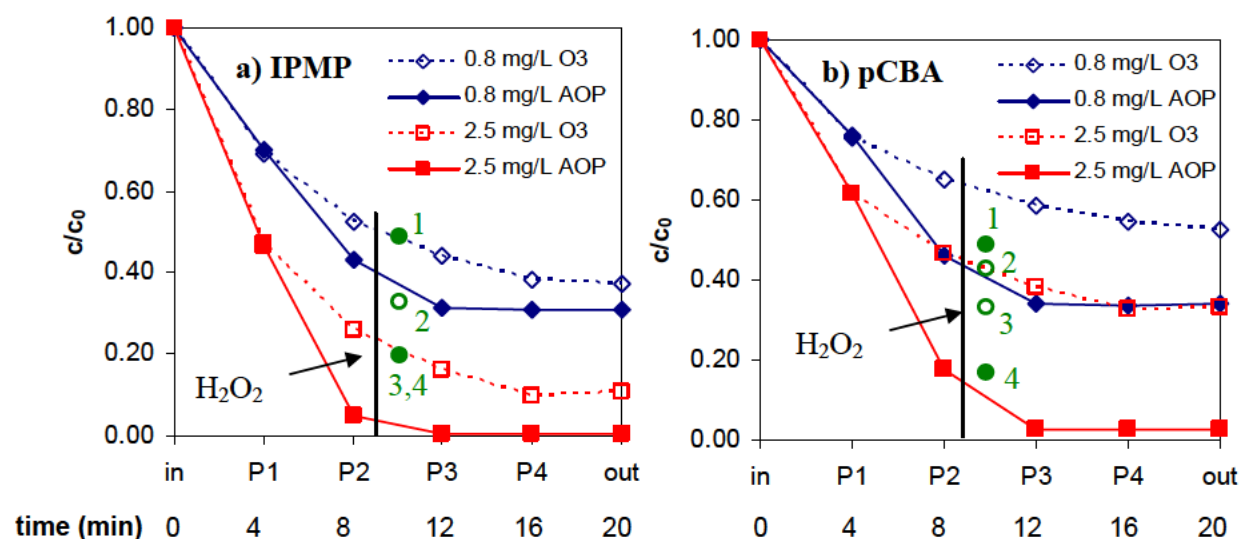


Figure 5-10: Transformation of IPMP (a) and pCBA (b) in pilot-scale experiments during conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$. O_3 : conventional ozonation; AOP: $\text{O}_3/\text{H}_2\text{O}_2$. Conditions: Lake Zurich water (pH 7.9; DOC 1.4 mg L^{-1} ; alkalinity 2.5 mM); 10°C . The corresponding residence time had been determined in tracer experiments (Fig. 5-2). Similar results as for pCBA can be expected for TCA and MIB due to the comparable reactivity towards ozone and $\cdot\text{OH}$. Initial concentrations: IPMP = $0.01 \text{ }\mu\text{M}$; pCBA = $1.5 \text{ }\mu\text{M}$. The green symbols represent a comparison with laboratory-scale data of IPMP (a) and TCA (b) (removal after 10 min; symbol 1: 1 mg L^{-1} AOP $\text{O}_3/\text{H}_2\text{O}_2$; 2: 1 mg L^{-1} conventional ozonation; 3: 2 mg L^{-1} conventional ozonation; 4: 2 mg L^{-1} AOP $\text{O}_3/\text{H}_2\text{O}_2$).

Calculations based on different hydraulic models and the measured ozone and estimated $\cdot\text{OH}$ exposures (eq 1) revealed that the removal of the T&O compounds could be reliably predicted [14]. A comparison between the calculated and the measured transformation of IPMP in the pilot ozonation reactor is shown in Fig. 5-11. The calculation revealed that the choice of the hydraulic model has little influence on the calculated concentrations for compounds which undergo transformation in the reactor. In the case of IPMP, the calculated transformation was mainly governed by the ozone and $\cdot\text{OH}$ exposures (eq 1). Therefore, the reactor could be described with a hydraulic plug-flow model.

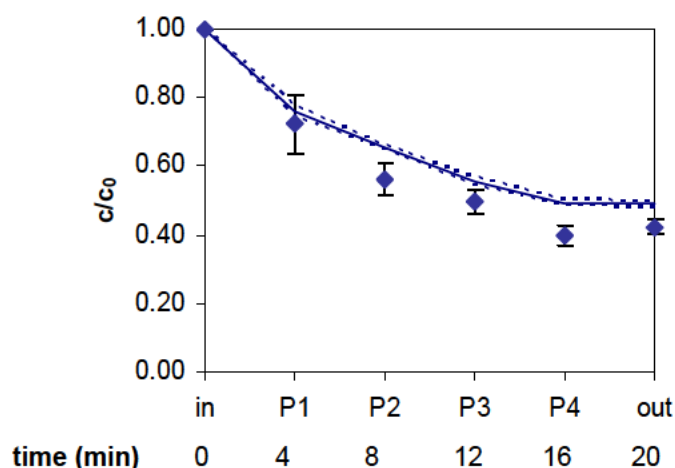


Figure 5-11: Measured and calculated transformation of IPMP in pilot-scale experiments. Symbols represent measured concentrations, the lines calculated oxidation using eq 1 and different hydraulic reactor models. The error bars represent the 95% confidence intervals of the five-fold analysis of samples from each sampling point (symbols) and of the calculation with different hydraulic reactor models (lines). Initial concentrations: ozone: 0.7 mg L^{-1} ; IPMP: $0.01 \text{ }\mu\text{M}$. 10°C .

Another comparison of the transformations of IPMP and TCA in the laboratory-scale experiments and the pilot-scale experiments is given in Figure 5-12. The removal of the T&O compounds is plotted against the determined $\cdot\text{OH}$ exposure. Please note that isoborneol data were plotted instead of TCA in the pilot-scale experiments because TCA was not spiked in these experiments. Due to their comparable reactivity towards ozone and $\cdot\text{OH}$, though, isoborneol and TCA are expected to behave similarly during ozonation. Figure 5-12 reveals a better correlation between laboratory-scale and pilot-scale experiments in the case of TCA (isoborneol) and less correlation for IPMP. This can be explained with the different temperature (ambient temperature in laboratory-scale and 10°C in pilot-scale experiments) and different degree of ozone consumption in the experiments. As IPMP reacts to a

substantial degree with ozone in conventional ozonation (Fig. 5-6), a comparison of different experiments based on the $\cdot\text{OH}$ exposure has its limitations. Furthermore, the reactivity of most organic compounds towards ozone shows a temperature dependence in the range of 35 - 50 kJ mol^{-1} [15], which means that a temperature increase of 10°C approximately doubles the reaction rate. In the case of TCA, which does not react with ozone, only the $\cdot\text{OH}$ exposure and the second order reaction rate constants between TCA and $\cdot\text{OH}$ determined the transformation of the compound. Furthermore, reaction rate constants with $\cdot\text{OH}$ are less temperature dependent than the respective ozone reaction rate constants.

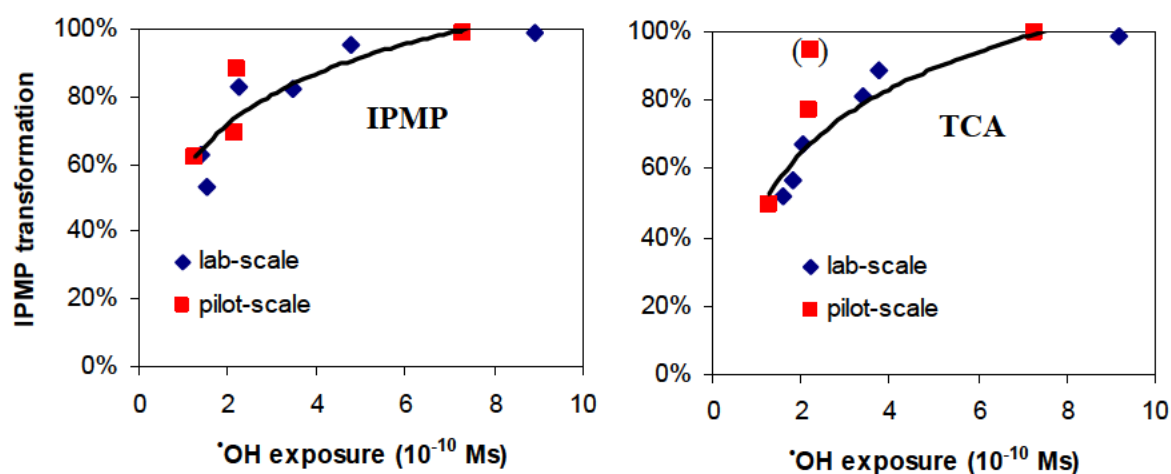


Figure 5-12: Comparison of the transformations of IPMP and TCA with respect to $\cdot\text{OH}$ exposure in laboratory-scale and pilot-scale experiments. Trendline: logarithmic correlation through the data from laboratory-scale and pilot-scale experiments. Laboratory-scale: Endpoints of conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$ after 10 min reaction time, $20\text{--}25^\circ\text{C}$; pilot-scale: endpoints of conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$ at the reactor outlet (20 min reaction time), 10°C . In pilot-scale experiments, isoborneol was used instead of TCA (comparable due to similar reactivity towards ozone and $\cdot\text{OH}$).

Bromate formation

The bromate formation in the pilot-scale experiments during ozonation of spiked Lake Zurich water (bromide level: $80\ \mu\text{g L}^{-1}$) is shown in Figure 5-13 for conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$. In contrast to the bench-scale experiments, there are only minor differences between conventional ozonation and the AOP $\text{O}_3/\text{H}_2\text{O}_2$ (Fig. 5-7). Bromate formation was especially prominent in the first few minutes after ozone addition, followed by a minor increase after sampling point P2.

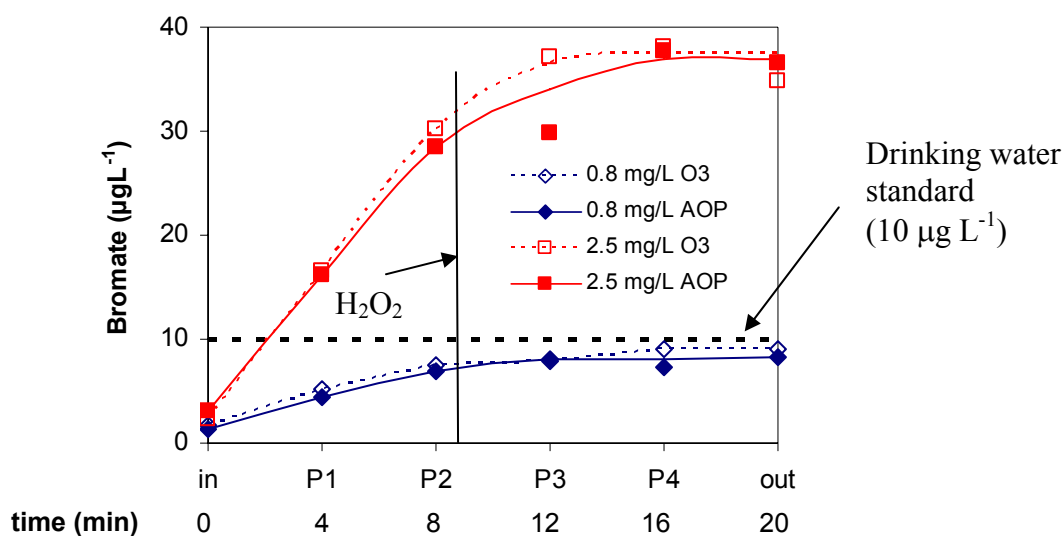


Figure 5-13: Bromate formation in pilot-scale experiments during ozonation and the AOP O₃/H₂O₂. O₃: conventional ozonation; AOP: O₃/H₂O₂. Conditions: spiked Lake Zurich water (pH 7.9; DOC 1.4 mg L⁻¹; alkalinity 2.5 mM; bromide level 80 µg L⁻¹); 10°C. The corresponding residence time had been determined in tracer experiments (Fig. 5-2).

Table 5-4 gives an overview of the bromate formation, T&O removal and disinfection potential for conventional ozonation and the AOP O₃/H₂O₂ in the pilot-scale experiments. The data reveal that the AOP O₃/H₂O₂ exhibits a higher T&O removal efficiency for a given ozone dose. Due to the late dosing of H₂O₂ in the AOP O₃/H₂O₂, the loss of disinfection potential compared to conventional ozonation is not very high. Furthermore, higher initial ozone doses could be applied in the AOP O₃/H₂O₂ without running into problems with residual ozone. However, with respect to bromate formation, the AOP O₃/H₂O₂ does not directly offer advantages over conventional ozonation. In the case of Lake Zurich water, the AOP O₃/H₂O₂ with an ozone dose of 2.5 mg L⁻¹ resulted in a reduction of more than 98% of the investigated T&O compounds and a bromate level that was just within the drinking water standard (10 µg L⁻¹). Yet, bromide levels in the raw water are subject to seasonal changes and can fluctuate a few µg L⁻¹ around the usual 20 µg L⁻¹ in Lake Zurich. This means that in the investigated pilot plant, the maximal ozone doses should not exceed about 2 mg L⁻¹ to guarantee low bromate levels.

TABLE 5-4. Bromate formation, T&O removal and disinfection potential during ozonation of Lake Zurich water in pilot-scale experiments

	ozone dose in conventional ozonation		ozone dose in AOP O ₃ /H ₂ O ₂	
	0.8 mg L ⁻¹	2.5 mg L ⁻¹	0.8 mg L ⁻¹	2.5 mg L ⁻¹
ozone exposure^a (Ct in mg L⁻¹·min)	7.9	32.6	5.4	15.2
Initial bromide	bromate concentrations at the outlet of the ozone reactor (µg L⁻¹)			
20 µg L ⁻¹	2.1	11.5	1.6	10.0
80 µg L ⁻¹	9.1	36.5	8.3	34.8
T&O compound	T&O removal in the ozone reactor			
IPMP	62%	88%	69%	>99%
pCBA ^b	46%	68%	67%	98%
β-ionone	>99%	>99%	>99%	>99%
organism	disinfection potential in the ozone reactor (log inactivation units)			
Cryptosporidium parvum ^c	0.80 (84%)	3.28 (99.95%)	0.55 (72%)	1.53 (>97%)
Giardia lamblia ^d	>4 (>99.99%)	>4	>4	>4
Viruses ^d	>4 (>99.99%)	>4	>4	>4

^a Fig. 5-9a^b proxy for MIB and TCA due to similar reactivity with ozone and ·OH^c at 10°C; calculation according to U.S. EPA: $(0.0397 \times (1.09757)^{T(\text{in } ^\circ\text{C})}) \times \text{Ct}$ [16]^d at 10°C; according to U.S. EPA [17]

5.4 Conclusions

The principle results showed good agreement between the laboratory-scale and pilot-scale experiments. This is especially true for the removal of T&O compounds which mainly react with $\cdot\text{OH}$. The good correlation between the experimental values from lab-scale and pilot-scale studies implies that the removal of compounds with little reactivity towards ozone can be estimated successfully based on laboratory data. This means that the usually time-intensive experiments on pilot- or full-scale plants can be limited to the determination of kinetic data in the laboratory at the temperatures of the larger scale reactors and to the determination of the $\cdot\text{OH}$ exposure in the pilot- or full-scale plant. With respect to bromate formation and the removal of T&O compounds with a higher reactivity towards ozone, though, the outcome of the pilot plant experiments can be compared with the bench-scale results to a limited extent only due to the different experimental setting (later dosing of hydrogen peroxide).

The experiments showed that in conventional ozonation as well as in the AOP $\text{O}_3/\text{H}_2\text{O}_2$ ozone doses higher than 2 mg L^{-1} were needed for a 99% removal of slow reacting T&O compounds. These results were obtained in Lake Zurich water, which is relatively low in DOC. Hence, it can be expected that in many cases even higher ozone doses are needed due to higher DOC-levels.

Furthermore, the laboratory experiments showed that with the addition of H_2O_2 the time needed for a certain removal of T&O compounds could be decreased by approximately one order of magnitude compared to conventional ozonation. Theoretically, this would allow the water utilities to design much smaller ozone reactors. However, in practical applications, where ozone often acts as an oxidant and a disinfectant, a certain ozone exposure (Ct-value) has to be guaranteed for disinfection. A feasible compromise has been illustrated with the pilot-scale experiments, where the first part of the ozone reactor was operated conventionally, followed by an AOP after the addition of H_2O_2 . This means that existing ozone reactors can be upgraded quite easily to function as AOPs. By adding H_2O_2 in the middle of the reactor, the oxidation capacity of the system can be enhanced whenever needed without losing too much of the disinfection potential.

However, in this setting there is hardly any advantage in bromate formation compared to conventional ozonation. If ozone doses higher than 1 mg L^{-1} are needed to achieve the desired oxidation and disinfection in waters with elevated bromide levels (higher than approximately $50 \text{ } \mu\text{g L}^{-1}$), bromate is likely to be formed at concentrations which exceed the drinking water

standard of $10 \mu\text{g L}^{-1}$. In these cases, bromate reduction strategies such as pH depression, ammonia addition or the chlorine-ammonia process could be applied prior to ozone addition [18, 19]. Despite all these reduction possibilities, a water utility which has to deal with high bromide levels will probably choose treatment options which work without ozone. In this context, UV-based treatment can be an interesting alternative because no bromate is formed in this process [2] and a fast oxidation of T&O compounds can be achieved with an adjustable addition of H_2O_2 . However, energy costs can be very high because a much higher UV-fluence is needed for the oxidation in UV-based AOPs than for UV-disinfection [20].

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Chapter 6

Taste and Odor Problems Generated in Distribution Systems

A Case Study about the Formation of 2,4,6-trichloroanisole

Abstract

A taste and odor (T&O) episode in a Swiss town, where consumers complained about a musty odor in their drinking water, was investigated. The application of a combined organoleptic and instrumental method for T&O analysis allowed to identify 2,4,6-trichloroanisole (TCA) in the drinking water. The absence of this compound in the untreated water showed that it was formed in the distribution system. TCA in tap water reached concentrations of up to 24 ng L⁻¹. Experiments conducted in the laboratory showed that the addition of low chlorine doses as residual disinfectant and biofilms in the distribution system played a key role in the formation of TCA. Based on these results, appropriate counter-measures, such as water distribution without a residual disinfectant and maintenance of household particle filters, could be taken to mitigate the T&O problem.

6.1 Introduction

As depicted in Chapters 1 and 3, many taste and odor (T&O) problems in drinking water are provoked by algal metabolites. 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 (Chapters 1, 4 and 5). However, some T&O complaints can not be related to the classical algal metabolites such as geosmin or 2-methylisoborneol (MIB), but are generated in the distribution system [1]. 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 flavors to the drinking water, which are often reported as plastic/rubber smells [2]. On the other hand, microbial activity in the distribution system (biofilms) can lead to the formation of a variety of T&O compounds [3].

Distribution generated T&O problems are a major concern to drinking water utilities because the respective T&O compounds can not be retained through treatment, but are directly delivered to the costumers. In these cases, it is of outer-most importance to identify the compounds that caused the problems and also to track their origins and formation mechanisms. Only then can counter-measures be applied to mitigate the problem.

In this chapter, the case study of a Swiss town which was confronted with consumer complaints is presented in detail. In this town, which is situated at 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 odor in their drinking water. Finally, we could identify 2,4,6-trichloroanisole (TCA) as the compound that provoked the complaints. On the basis of this case, this chapter illustrates a possible procedure for water utilities which are confronted with T&O complaints. This chapter includes the identification of the responsible T&O compound and its origin as well as the description and evaluation of counter-measures.

6.2 Materials and Methods

6.2.1 Water treatment plant (WTP)

The water utility in the investigated area treats water from Lake Zurich and distributes it to three municipalities with a total population of about 30'000 habitants. Lake Zurich (pH 7.9; DOC 1.4 mg L⁻¹; alkalinity 2.5 mM) is mesotrophic and normally shows an annual lake turnover from December to March. Figure 6-1 gives a simplified overview of the treatment train which has been in operation since December 2005 and 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 had changed the drinking water treatment regime. Sodium hypochlorite had been applied as residual disinfectant until May 2007. The residual concentration of active chlorine was in the range of 0.02 - 0.06 mg L⁻¹.

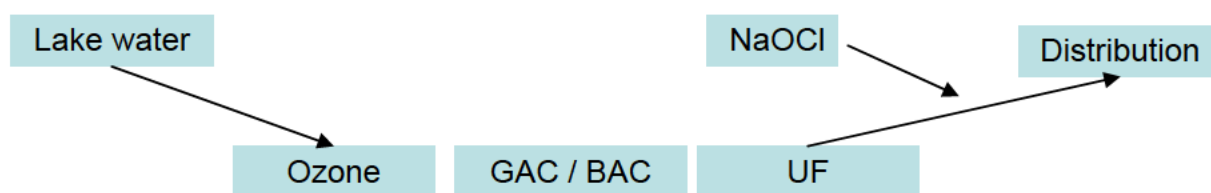


Figure 6-1: Treatment scheme of lake water in the investigated WTP since December 2005. GAC / BAC: granular activated carbon (biologically active); UF: ultrafiltration; NaOCl: sodium hypochlorite (residual disinfectant for distribution system).

6.2.2 Sampling sites

Figure 6-2 gives a simplified overview of the sampling sites in this case study. Sampling points #6 and #8 are hydrants in the vicinity of home 1 and 2; sampling points #7 and #9 indicate tap water samples inside the respective houses. If not indicated otherwise, these four sampling points were sampled after approximately five minutes of pre-flushing to allow the water temperature to stabilize.

At sampling point “f”, water was taken from a fountain where water was running constantly. Due to the long transport stretch from the WTP, this point was a good representation for the average distribution system.

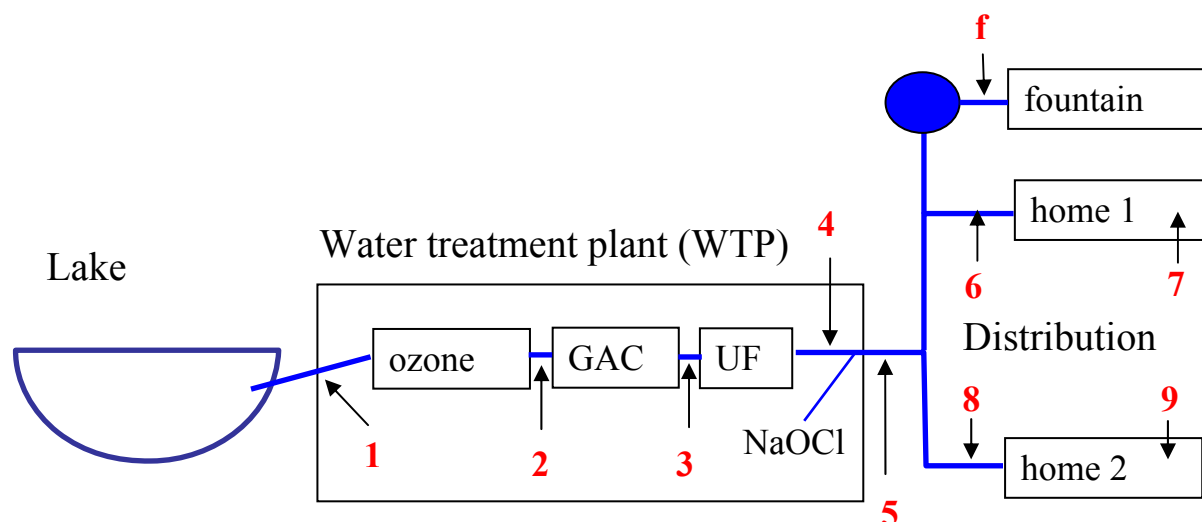


Figure 6-2: Sampling sites in this case study. Sampling points: #1: raw water; #2-#5: WTP; #6, #8: hydrants; #7, #9: houses; f: fountain

6.2.3 Analytical methods

Sensory analysis. Treated water (site #5; Fig. 6-2) and water samples from several points in the distribution system were analyzed 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 odor 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 (Chapter 2).

Microbiological methods. Total cell numbers and the assimilable organic carbon (AOC) were monitored during the investigation period. A detailed description of these flow-cytometry based methods can be found in refs. [4, 5].

6.2.4 Sampling and experiments to solve the case

Table 6-1 summarizes the investigations which were performed to track the T&O compounds. The first samples after the complaints were analyzed by the sensory panel of the laboratory of the Canton of Zurich. Approximately one year after the complaints started, several samples from the source (lake water) to the tap (Fig. 6-2) were specifically analyzed for T&O compounds using the combined SPME-GC-MS/ODP method (Chapter 2). To identify the role

of biofilms in the formation of the identified T&O compounds, a particle filter of one of the investigated homes was dismantled and used for laboratory experiments. In these experiments, water from the WTP after ultrafiltration (site #4, Fig. 6-2) was used unaltered or spiked with suspected precursors (see result section for details). The water was kept in the filter unit at room temperature and sampled five times within a month. The samples were filtered with 0.45 µm Nylon syringe filters (BGB; Switzerland) and stored at 4°C. In addition to these experiments, the formation of the suspected precursors during chlorination was modeled by using the computer program Acuchem, a tool for the kinetic simulation of complex reaction systems [6].

TABLE 6-1. Chronology of events and investigations

Date	Event
Dec 2005 / Jan 2006	Change in operation of WTP (Fig. 6-1); first complaints after a few weeks
Dec 2005 – Feb 2008	Sensory analysis of treated water on a bi-weekly to monthly basis
Nov 2006	Sampling at the WTP and T&O screening with SPME-GC-MS/ODP (before lake turn-over)
Feb 2007	Sampling at the WTP and T&O screening with SPME-GC-MS/ODP (during lake turn-over)
March 2007	Sampling at two homes and T&O screening with SPME-GC-MS/ODP
May 2007	Stop of the addition of residual disinfectant (NaOCl) at the WTP
June 2007	Sampling at two homes (the same ones as in March 2007) and T&O screening with SPME-GC-MS/ODP
Nov 2007 - Feb 2008	Experiments with particle filter from one of the investigated homes

6.3 Results and Discussion

6.3.1 Sensory analysis of drinking water

After the first complaints in December 2005, several samples were analyzed by the sensory panel. While the treated water after the WTP (site #5, Fig. 6-2) exhibited a normal taste to most of the examiners, the majority of the panel confirmed the musty odor in the drinking water at the fountain (site “f”, Fig. 6-2). Figure 6-3 summarizes the olfactory findings for these two sampling points.

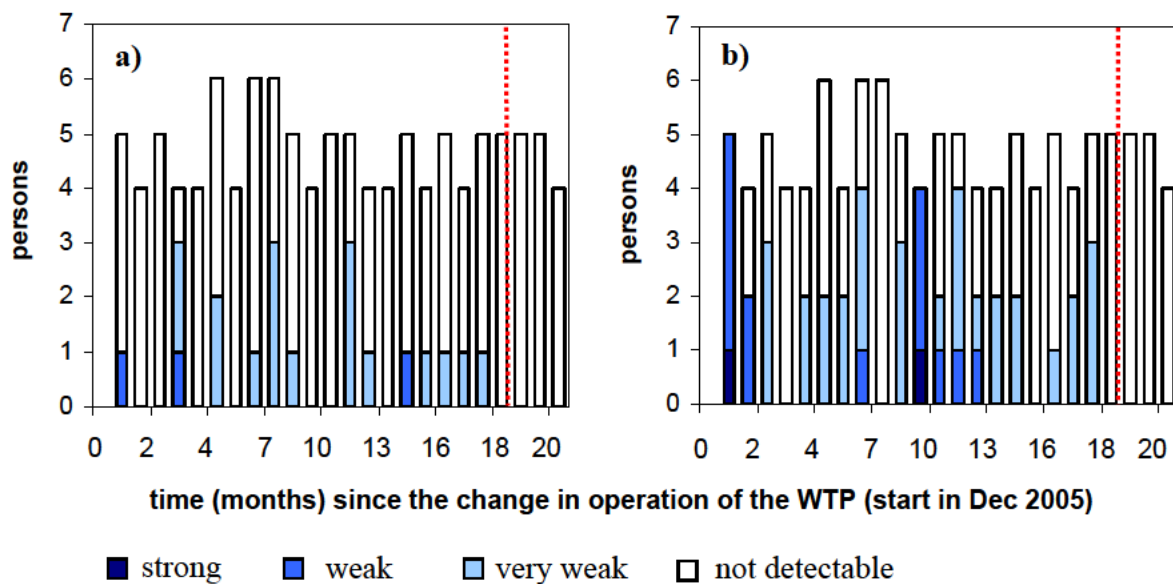


Figure 6-3: Sensory analysis of treated water at WTP site #5 (Fig. 6-2) (a) and at the fountain “f” (b). The analysis has been performed on a bi-weekly to monthly basis since the start of the new WTP (Dec 2005). The red dotted line indicates the end of the addition of residual disinfectant in May 2007 (NaOCl).

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 (odor threshold: 0.025 mg L⁻¹ [7]). 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 prior to the change in operation. Indeed, in the old treatment train the water was first subjected to

filtration, whereas in the new procedure the raw water was directly ozonated without a pre-filtration step (Fig. 6-1).

Figure 6-3b shows that the musty odor was detected by the sensory panel mainly in two periods, namely at the very beginning of the new operation scheme (Dec 05 – Jan 06) and in summer – fall 2006. A higher temperature in the distribution system (15-20°C in summer months compared to <10°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 generally is very abundant in the metalimnion in fall (Chapter 3), 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.

6.3.2 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 of several sampling campaigns were specifically analyzed for T&O compounds with SPME-GC-MS/ODP.

In two campaigns, the WTP at points #1 - #5 (Fig. 6-2) and a fountain (site “F”) were sampled. No T&O compounds could be detected in the first campaign, which was run in Nov 2006 before the turn-over of Lake Zurich. The second campaign, which was performed in Feb 2007 during the lake turn-over, revealed the presence of two T&O compounds in the raw water (musty 2-methylisoborneol with an odor threshold of 15 ng L⁻¹ and fruity β-cyclocitral with an odor threshold of 19'000 ng L⁻¹ (Chapter 1)). However, the concentrations were already below the quantification limit (< 2 ng L⁻¹) and the respective odor threshold concentrations in the raw water and not detectable after treatment. Therefore, these compounds could not be responsible for the musty odor 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 (points #6 and # 8, Fig. 6-2) in the vicinity of the homes were sampled together with the tap water (points #7 and # 9, Fig. 6-2) inside the houses.

During this sampling campaign, a 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 odor threshold of 30 pg L^{-1} [8]. Table 6-2 shows the corresponding results of this investigation in March 07 at the tap of the costumers.

TABLE 6-2. Concentrations of TCA at the fountain, two hydrants and in two private homes with and without addition of residual disinfectant; in ng L^{-1} ^a

sampling point	With chlorine (March 07)	Without chlorine (June 07) ^d
„f“ fountain	n.d. ^b	n.d. ^b
#6 hydrant home 1	n.d. ^b	n.d. ^b
#7 tap water home 1	23.6 ± 2.8	n.d. ^b (7 ng L^{-1}) ^c
#8 hydrant home 2	6.4 ± 2.9	n.d. ^b
#9 tap water home 2	4.9 ± 3.0	n.d. ^b

^a errors = 95% confidence intervals calculated from the calibration with five external standards

^b n.d. = not detectable, i.e., $< 2 \text{ ng L}^{-1}$

^c in brackets: concentration, immediately after the tap was opened; all the other samples of home 1 and home 2 were taken after a flushing period of five minutes (Chapter 6.2.2)

^d five weeks after the addition of chlorine had been stopped

Table 6-2 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. Indeed, the water temperature at this point was usually $3\text{--}5^\circ\text{C}$ higher than in other places 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.

6.3.3 Hypothetical mechanism of TCA-formation

Figure 6-4 shows the supposed formation mechanism of TCA in this case 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 a biomethylation of chlorophenols, has been described in literature [9]. It is likely that this process led to the TCA that was observed in the two investigated houses.

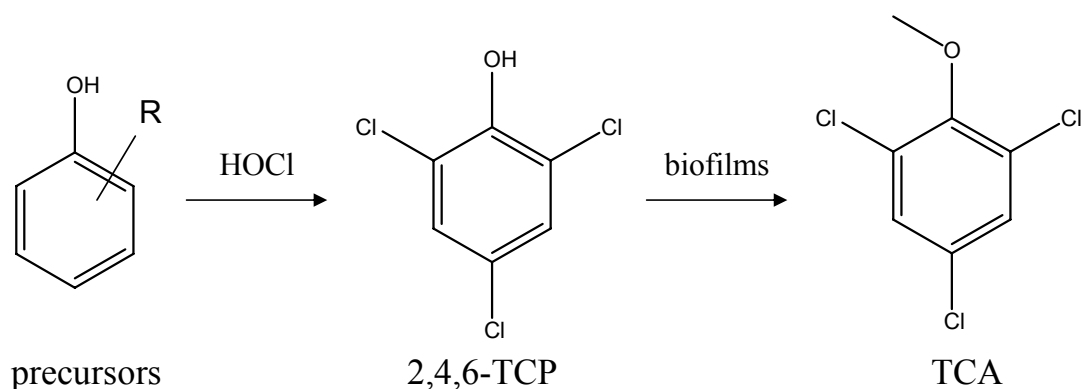


Figure 6-4: Simplified formation mechanism of TCA in the distribution system. TCP: trichlorophenol

We speculated 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 the electrophilic substitution mechanism [10]. A complete chlorination with an eventual cleavage of the aromatic ring is suspected at substantially higher chlorine doses than were used in the WTP (less than 0.1 mg L^{-1} active chlorine). To confirm 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. The kinetic data for the model are summarized in Table 6-3.

TABLE 6-3. Second-order rate constants for reactions of HOCl with deprotonated chlorophenols

compound	pK _a	k (M ⁻¹ s ⁻¹) ^a	oxidation products
phenol	10.0	30'000	80% 2-chlorophenol; 20% 4-chlorophenol
2-chlorophenol	8.6	24'000	74% 2,6-dichlorophenol; 26% 2,4-dichlorophenol
4-chlorophenol	9.4	26'000	2,4-dichlorophenol
2,4-dichlorophenol	7.9	300	2,4,6-trichlorophenol
2,6-dichlorophenol	7.0	190	2,4,6-trichlorophenol
2,4,6-trichlorophenol	6.2	13	2,3,4,6-tetrachlorophenol

^a second order rate constants obtained from refs [11, 12]; the reactions of protonated phenols with HOCl are negligible at pH 8 and therefore, were not taken into account for the calculations

The calculated formation of TCP with different initial chlorine doses is shown in Figure 6-5. The calculations revealed that chlorine doses between 0.05 and 0.5 mg L⁻¹ Cl₂ led to high amounts of TCP. Stable TCP concentrations were achieved after approximately 20 hours due to the consumption of chlorine. 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 one hour for a chlorine dose of 1 mg L⁻¹ or 2 mg L⁻¹. With an assumed chlorine half-life time of five hours in the WTP-effluent water, 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) [12]. Therefore, the optimum chlorine dose has to be carefully adjusted to case-specific conditions.

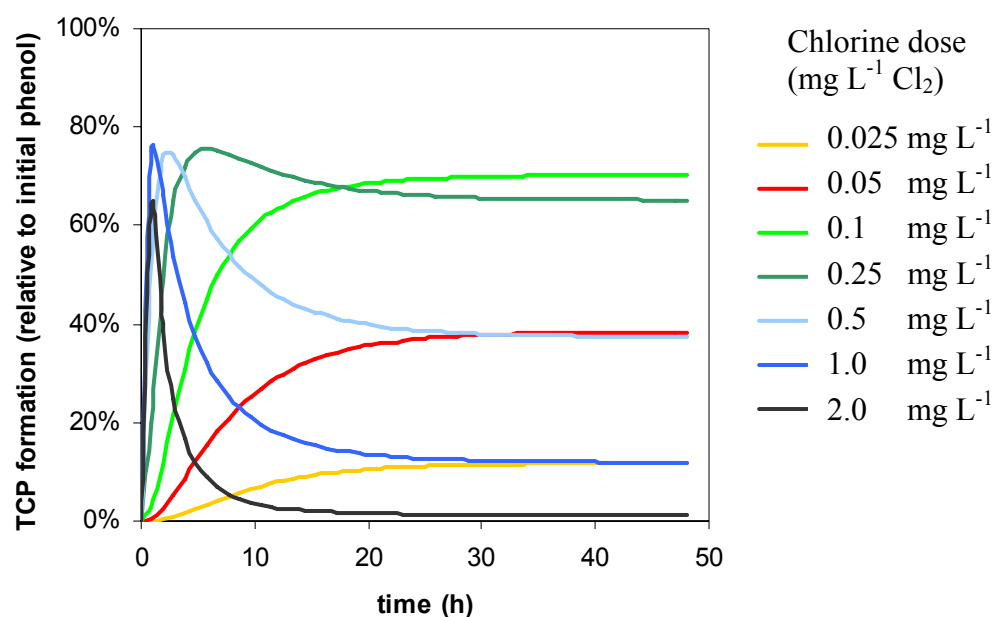


Figure 6-5. Calculated formation of 2,4,6-trichlorophenol (TCP) during the chlorination of phenols with different initial chlorine concentrations. The rate constants for the formation of the chlorophenol species are summarized in Table 6-3. A half-life time of five hours for chlorine in the WTP-effluent water was assumed in the model.

Despite these obvious reactions of phenols to TCP and further on to TCA, it remains unclear 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 imbedded 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 [13]. Indeed, Figure 6-6 reveals that approximately one month after the change in operation (December 2005), the spectral absorption coefficient (SAC 254nm) for the treated water started to rise. The SAC 254nm is an indicator for the presence of aromatic compounds in the water. Obviously, the activated carbon filter could not completely retain the aromatic compounds for more than a few weeks. 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.

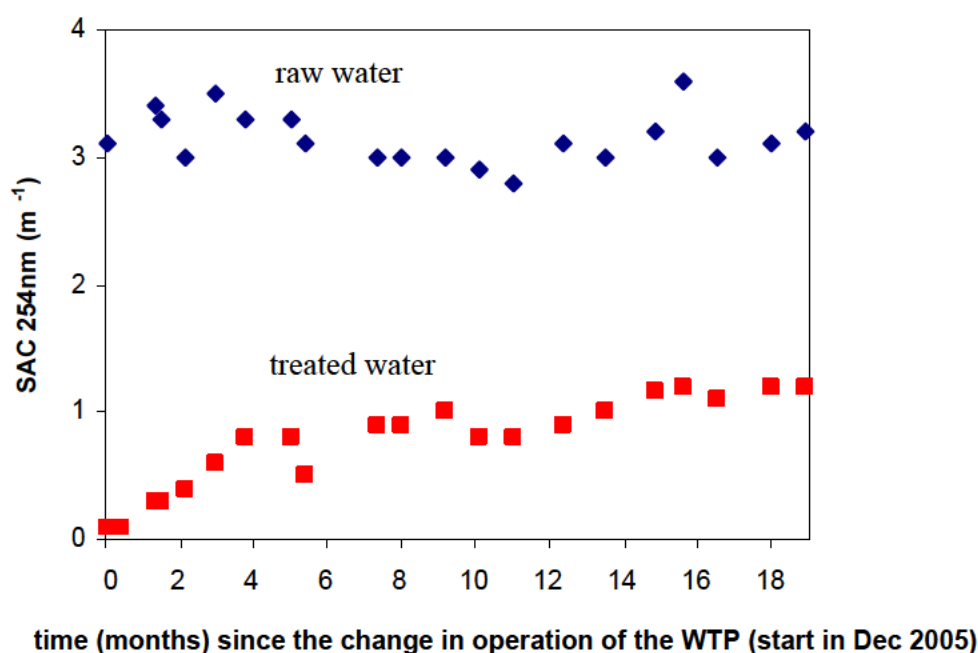


Figure 6-6: Spectral absorption coefficient (SAC) at 254nm of raw water and treated water. Raw water: sampling point #1 (Fig. 6-2); treated water: sampling point #5

6.3.4 Mitigation strategy

According to our hypothesis (shown in Fig. 6-4), 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 analyzing 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 missing chlorine did not lead to an increase in the bacterial cell numbers (data not shown), which can be explained with the low AOC-levels (assimilable organic carbon) of the treated water ($15 - 30 \mu\text{g L}^{-1}$). Hence, the hygienic 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 07 data in Table 6-2 show the results that were obtained five weeks after chlorine dosage had been stopped. TCA was not detected in the distribution system anymore. 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 odor after May 2007 (Fig. 6-3). Consistently, the consumer complaints declined, although they did not cease completely.

6.3.5 The role of the biofilm

To investigate whether the formation of TCA was mediated by biofilms, the particle filter of home 1 was dismantled and used for laboratory experiments. In a first experiment, water from the WTP after ultrafiltration (site #4, Fig. 6-2) 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 $10 \mu\text{g L}^{-1}$. In a final 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). After the addition of chlorine, the water was stored for four hours until it was transferred to the filter unit. This period represented the transportation time in the distribution system.

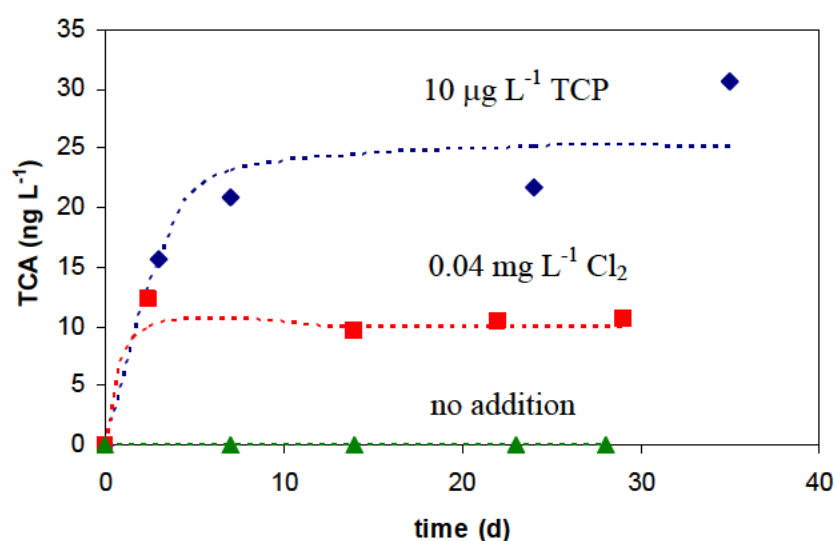


Figure 6-7: TCA formation in the particle filter from home 1 during laboratory experiments. Conditions: ultrafiltrated water from the WTP without the addition of assumed precursors (Fig. 6-4) and spiked with TCP or chlorine; 20°C.

Figure 6-7 shows the resulting TCA concentrations of the laboratory experiments with the household filter. No TCA formation could be observed with unspiked WTP-effluent water. The outcome of the experiment with TCP addition illustrates the transformation of TCP into TCA. The experiment with chlorine addition, which also led to TCA formation, indirectly confirms the formation of TCP after the addition of the residual disinfectant. The resulting TCA concentrations were similar as detected in the first sampling campaign in this home (24 ng L^{-1}). Hence, the important role of biofilms and the precursors (phenolic compounds and chlorine) in TCA formation could clearly be confirmed with these experiments.

6.4 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 phenolic 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 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:

- Low concentrations of chlorine as residual disinfectant ($< 0.5 \text{ mg L}^{-1}$) can favor the formation of TCA. Therefore, it is more appropriate to either distribute the water without the addition of chlorine or to dose higher amounts, which in turn can again lead to consumer complaints due to the chlorine taste of the water or lead to the formation of undesired trihalomethanes. In the former case, it is very important to monitor the microbiological quality in the distribution system. Towards this end, total bacterial cell counts are an ideal control parameter [4]. 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 low molecular weight polymer units that are easily bio-available. Biofilms can quickly establish on the surface of materials which release these compounds in high amounts. 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 the distribution system and in households.
- Particle filters that are used in households should be cleaned regularly. Otherwise, biofilms are likely to quickly 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 rigorously maintained.

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Chapter 7

General Conclusions

This study aimed at the identification of the most relevant taste and odor (T&O) compounds in surface waters in Switzerland and at the investigation of the removal of these compounds during drinking water treatment. A novel analytical approach which combined instrumental and olfactory detection was applied. This method with its parallel detection at the MS and the sniff-port allowed a fast and reliable detection and quantification of T&O compounds in natural water samples. Additionally, the extraction with headspace SPME (solid phase micro extraction) proofed to be very sensitive for the analysis of T&O compounds even in complex matrices such as phytoplankton. Detection limits for most of the investigated compounds were in the low ng L⁻¹-range with good linearity over two orders of magnitude.

In the course of this study, six T&O compounds could be identified in the three investigated lakes (Lake Greifensee, Lake Zurich and Lake Lucerne), though at relatively low concentrations (maximum concentrations of geosmin 19 ng L⁻¹, MIB 3 ng L⁻¹, β -ionone 27 ng L⁻¹, β -cyclocitral 7 ng L⁻¹, 2-isobutyl-3-methoxypyrazine 2 ng L⁻¹, 2-isopropyl-3-methoxypyrazine 16 ng L⁻¹). A general correlation to the phytoplankton biomass and therefore, elevated T&O concentrations in eutrophic water bodies during summer was confirmed. Furthermore, the study revealed that a substantial part of the investigated compounds was present in the water as particle-bound fraction. For the first time, the concentration of β -ionone in lake water has been shown to be largely influenced by the cyanobacterium *Planktothrix rubescens*.

Ozonation and activated carbon filtration are amongst the most powerful tools to mitigate surface-water related T&O problems during drinking water treatment. As for conventional ozonation, this study showed that this process was capable to oxidize most of the T&O compounds to more than 50% under typical drinking water ozonation conditions. However, the use of conventional ozonation is limited when slow reacting compounds have to be oxidized to a higher degree. This study showed that even for natural waters with low DOC-levels (Lake Zurich, DOC 1.4 mg L⁻¹) ozone doses higher than 2 mg L⁻¹ were needed to achieve a T&O removal of 90%. Higher ozone doses are likely to cause problems with high ozone residuals and oxidation by-products, such as AOC (assimilable organic carbon) and the potentially carcinogenic bromate. This study illustrated that the application of advanced oxidation processes (AOPs) could be appropriate in cases where an enhanced removal of T&O compounds is necessary. On the one hand, AOPs based on ozone/hydrogen peroxide

significantly shortened the time to achieve a certain T&O removal efficiency with a given ozone dose. On the other hand, these processes exhibited no ozone residuals and led to lower bromate formation due the reaction of intermediates with H_2O_2 back to bromide. Pilot-scale experiments revealed that real reactor systems can easily be upgraded to function as AOPs, which allows water utilities to quickly adapt to changes in the raw water quality.

In Switzerland, where T&O concentration in surface waters are rather low and where a multi-barrier approach is chosen to treat surface waters, it is unlikely that T&O problems could be generated by dissolved algal metabolites from lake waters. As for the particle-bound compounds, their removal or potential release during drinking water treatment is strongly dependent on the treatment processes, i.e., on the sequence of removal and oxidation processes. In the investigated Swiss lakes, though, the concentrations of particle-bound compounds are probably also too low to generate T&O problems. Nevertheless, future changes in the phytoplankton community might accentuate the production of particle-bound T&O compounds. Also in this context will it be necessary to extend the research on the release of intracellular T&O compounds during drinking water treatment.

According to the reasoning above, it can be concluded that most of the reported T&O problems in Switzerland can be traced back to chlorine residuals and other phenomena generated in distribution systems. Apart from compounds that leached from materials used in the distribution system, biofilm mediated reactions are likely to have caused several T&O problems. The presented case study on the formation of 2,4,6-trichloroanisole (TCA) confirmed this important role of biofilms. Three main triggers for TCA-formation were identified: (i) long residence time in the distribution system, (ii) biofilms in the distribution system and (iii) the availability of precursors (e.g. 2,4,6-trichlorophenol).

In contrast to Switzerland, many other countries are affected by T&O problems that can be traced back to algal metabolites, mainly geosmin and 2-methylisoborneol. This can be explained by the often poorer raw water quality, which in this context means more eutrophic water bodies with higher phytoplankton biomass, and less advanced drinking water treatment. Chlorine, for example, is still widely applied in drinking water treatment. Although it may fulfill the requests towards disinfection, its reactivity towards many T&O compounds is too low to prominently decrease T&O concentrations without additional treatment steps (such as activated carbon filtration). Under these circumstances, a good management of the water bodies that are used for drinking water purposes, i.e., a reduction of nutrient loads, and an

optimization or even change of drinking water treatment processes are the most promising measures towards a better organoleptic quality of the drinking water.

Concluding, it is important to note that it is not possible to give general recommendations about the mitigation of T&O problems because specific solutions have to be found for each case. This study can serve as a basis for solution of T&O problems by providing:

- An analytical method for a reliable detection and quantification of T&O compounds
- Improved knowledge of the treatment of surface water derived T&O compounds
- Mitigation strategies of T&O problems in distribution systems

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