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Final report

Consideration of disinfection by-products in the environmental risk assessment of biocidal products- Inventory & development of recommendations for the assessment

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Abstract: Consideration of disinfection by-products in the environmental risk assessment of biocidal products-Inventory & development of recommendations for the assessment

In the first part of the project, a compilation of data on disinfection by-products (DBPs) as well as the biocidal active substances from product types (PTs) 1-5, 11 and 12 that are approved within the EU or within the approval process were compiled. The data on the DBPs resulted from a literature search in which 272 DBPs were identified. In addition to the substance data, the active substances used and the matrix treated were recorded in the tabular summary. A strong bias of the scientific literature on the investigation of highly reactive, especially chlorinating active substances in aqueous solution was determined. The list of biocidal active substances was compiled from the ECHA database (as of July 2019). A categorization of the biocidal active substances was developed and the DBP formation potential of each active ingredient was evaluated on the basis of this categorization. In a modeling approach, the distribution of selected DBPs and biocidal active substances in the water and air compartments for applications in solution and on surfaces and the distribution in water and sewage sludge in a sewage treatment plant was estimated. In most cases, there were significant differences between the distributions of the DBPs and the active ingredients. The formation of approximately 60 DBPs was investigated in laboratory simulations of disinfection applications in solution and on surfaces with different active substances. In addition, samples from real disinfection applications were analyzed. Based on the project results, the current procedure for risk assessment of the DBPs was analyzed in the last project phase and proposals for modifications were discussed, which aim to simplify and harmonize the risk assessment of the DBPs within the EU.

Kurzbeschreibung: Berücksichtigung von Desinfektionsnebenprodukten im Rahmen der Umweltrisikobewertung von Biozid-Produkten - Bestandsaufnahme & Entwicklung von Empfehlungen für die Bewertung

Im ersten Teil des Projektes wurde eine Zusammenstellung von Daten zu Desinfektionsneben-produkten (DBPs) sowie den in der EU zugelassenen und im Zulassungsverfahren befindlichen bioziden Wirkstoffen aus den Produkttypen (PTs) 1-5, 11 und 12 erstellt. Die Daten zu den DBPs resultierten aus einer Literaturrecherche, bei der 272 DBPs identifiziert wurden. In der tabellarischen Zusammenfassung wurden neben den Substanzdaten die jeweils eingesetzten Wirkstoffe und die behandelte Matrix festgehalten. Hierbei wurde ein starker Fokus der wissenschaftlichen Literatur auf die Untersuchung stark reaktiver, vor allem chlorierender Wirkstoffe in wässriger Lösung festgestellt. Die Liste der bioziden Wirkstoffe wurde der ECHA Datenbank entnommen (Stand Juli 2019). Es wurde eine Kategorisierung der bioziden Wirkstoffe erarbeitet und anhand dieser Kategorisierung das DBP-Bildungspotential jedes Wirkstoffes bewertet. In einem Modellierungsansatz wurde die Verteilung ausgewählter DBPs und biozider Wirkstoffe in den Kompartimenten Wasser und Luft bei Anwendungen in Lösung sowie auf Oberflächen und die Verteilung in Wasser und Klärschlamm in einer Kläranlage abgeschätzt. Hierbei zeigten sich in den meisten Fällen signifikante Unterschiede zwischen den Verteilungen der DBPs und der Wirkstoffe. In Laborsimulationen von Desinfektionsanwendungen in Lösung und auf Oberflächen mit verschiedenen Wirkstoffen wurde die Bildung von ca. 60 DBPs untersucht. Zusätzlich wurden Proben aus reellen Desinfektionsanwendungen analysiert. Anhand der Projektergebnisse wurde im letzten Projektabschnitt die aktuelle Vorgehensweise zu Risikobewertung der DBPs analysiert und es wurden Vorschläge zur Modifikation diskutiert, die eine Vereinfachung und Harmonisierung der Risikobewertung der DBPs innerhalb der EU zum Ziel haben.

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List of abbreviations

AOX	Adsorbable organic halogen compounds
AR	Assessment Report
a.s.	Active substance
BCDMH	Bromochlorodimethylhydantoin
BDCAA	Bromodichloroacetic acid
BDCM	Bromodichloromethane
BPR	Biocidal Products Regulation
BWWG	Ballast Water Working Group
CAR	Competent Authority Report
CMIT	Chlormethylisothiazolinon
DBAA	Dibromoacetic acid
DBAN	Dibromoacetonitrile
DBCAA	Dibromochloroacetic acid
DBCM	Dibromochloromethane
DBP	Disinfection by-product
DCAA	Dichloroacetic acid
DNPH	Dinitrophenylhydrazine
DPN	Dalapon
DT50	Dissipation time for 50% of the original amount (half life)
ECHA	European Chemicals Agency
ERA	Environmental Risk Assessment
EU	European Union
GC-MS	Gas chromatography mass spectrometry
GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection
HAA	Halogenacetic acid
HAcAM	Haloacetamides
HAL	Haloacetaldehydes
HAN	Haloacetonitrile
HAM	Haloacetamides
HBQ	Halobenzochinones
HK	Haloketones
HNM	Halonitromethanes
IMO	International Maritime Organization
I-THM	Iodo-Trihalomethanes
Kaw	Partition coefficients between water and air
Koc	Partition coefficients between water and soil

LC-MS	Liquid chromatography mass spectrometry
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MDL	Method detection limit
MIT	Methylisothiazolinon
MoA	Mode of action
MS	Member State
NA	Nitrosamines
n.d.	Not detected
NDMA	N-Nitrodimethylamine
n.m.	Not measured
PBT	Persistent, bioaccumulative and toxic
PEC	Predicted environmental concentration
PNEC	Predicted no effect concentration
PT	Product Type
QSAR	Quantitative structure-activity relationship
STP	Sewage treatment plant
TBAA	Tribromoacetic acid
TBM	Tribromomethane
TCAA	Trichloroacetic acid
TCAL	Trichloroacetaldehyde
TCM	Trichloromethane
THM	Trihalomethanes
TOC	Total organic carbon
WET	Whole effluent testing
WP	Work package

Summary

The environmental risk assessment (ERA) following the precautionary principle is a main element of the EU Biocidal Products Regulation 528/2012 (EU, 2012; BPR). Disinfectants and preservatives in industrial processes, the topic of this study, are biocidal products covered by the BPR. Their mode of action comprises different principles, including a high chemical reactivity of some biocidal active substance (a.s.). Possible reaction products generated during their use must also be included into the ERA of the concerned biocidal a.s. or biocidal products. The procedure for the ERA of those so-called disinfection-by-products (DBPs) is described in the Guidance on Disinfection By-Products (ECHA, 2017). However, this guidance still has its limitations and discussions on how to conduct ERA of DBP are ongoing. Furthermore, it is limited to halogenated DBPs and the product types (PTs) 2, 11 and 12. As a consequence, a harmonized science-based ERA of DBPs is currently not conducted which may hamper the mutual recognition of product approvals between member states.

The present project aimed to compile existing data on DBPs and biocidal a.s. from relevant PTs, which are approved within the EU or are within the approval process. PTs relevant for the project were defined to be PTs 1-5, 11 and 12. Within these PTs, a.s. might come in contact with organic matrices and the generated DBPs may enter the environment and thus may be relevant with respect to an ERA of the biocidal a.s.. Furthermore, the goal was to check the relevance of the identified DBPs for the ERA by estimating potential entry routes into the environment and by analysing samples from both laboratory disinfection simulations and genuine applications. Based on the achieved results, changes and amendments of the actual ERA process for DBPs were proposed.

Literature search on DBPs

The literature search on DBPs was performed for a time period of 2013 to April 2019, also including selected publications before 2013 referenced in newer literature. Of almost 3000 search results, 154 were selected as relevant by screening titles and abstracts. Studying the selected literature, 272 DBPs were identified, 186 of them being halogenated and 86 being non-halogenated. The detailed results of the literature review were compiled in Excel sheets including DBP data (name, molecular structure, molecular formula and CAS No., formation conditions, name and CAS No. of applied biocide active substance and treated matrix).

However, the outcome of the literature search on DBPs with respect to the targets of the project was only limited due to several specific characteristics of almost all literature on DBPs. A main limitation was the focus of existing studies on only very few highly reactive molecules. Approximately 90% of the investigated a.s. were acting by chlorination and the remaining approx. 10% by oxidation. Consequently, the DBP mentioned in literature comprise only relatively small molecules, typical breakdown products resulting from the effect of the highly reactive a.s.. No information on particular DBPs generated by other, less reactive biocidal a.s., for example carbonyl compounds, was found, although a DBP formation is generally well possible. Furthermore, the literature focused not on specific regulatory defined biocidal a.s. but rather on a reaction type like chlorination or oxidation. As a consequence, only limited information was available based on literature to analyse the DPB forming potential of regulatory defined biocidal a.s. and a direct assignment of DBP to particular biocidal a.s. was not possible. Finally, no literature focusing on DBP formation during disinfection of surfaces was found. All searched literature describes experiments in aqueous solutions, but in absence of water the generated DBPs may differ.

The conditions under which DBP are formed are strongly dependent on a large variety of factors, which is why no general statements on factors influencing their generation could be drawn from literature. Based on the results of the literature search, there is no general trend for certain DBP classes or individual representatives. To this point, the results of the literature search were not sufficient to draw conclusions on specific DBP that would suffice to be considered during the assessment of specific use conditions and whose solitary assessment would follow the precautionary principle.

DBP formation potential of biocidal a.s.

A list of biocidal a.s. belonging to the PTs, which are either approved within the EU or within the approval process (status in July 2019) was prepared using the ECHA database. The resulting list comprised 32 approved a.s. and 94 a.s. within the approval process. Basic data about the a.s. (molecular formula and structure, CAS-No, PT) and additional information about potential for the formation of DBPs based on expert judgement were compiled.

However, the types and amounts of DBP resulting from their use cannot be generally estimated based on specific categories such as the PT in which an a.s. is assessed. Although the organic matter in the matrix within the regarded PTs, will generally have comparable constituents, the concentration and detailed composition will differ to a large extent between the PTs but also between particular uses within the same PT. Additionally, presence and amount of water can also be an important factor for DPB formation and lead to different reactions and change of the type of DBP produced.

Two approaches of a categorisation with respect to the DBP forming potential were developed for the regarded biocidal a.s., one based on the mode of action and another one according to the chemical structures of the biocidal a.s.. Categorisation by mode of action turned out to be quite complex in detail, while the second approach proved to be suitable for the project. As a result of expert judgement and the categorisation, 57 out of 126 biocidal a.s. were rated to have relevant potential for the formation of DBPs.

The categories by chemical structure of the a.s. were then linked to specific DBP found in literature. This bypass, linking DBP to categories instead of to specific biocidal a.s. was necessary because literature studies usually only stated reaction types (e.g. chlorination or oxidation) instead of specific a.s. (see above). However, the results now allow to narrow down expected DBP for specific a.s. based on their categorisation.

Entry routes into environment

Assuming that one reason a DBP requires a separate ERA is whether it partitions differently into the environmental compartments compared to the biocidal a.s., a basic modelling approach was used to estimate possible entry routes of selected DBPs and biocidal a.s. into the environment. The modelling mainly focused on the question whether the entry routes for DBPs and biocidal a.s. are differing or not. Using calculated air – water distribution coefficients (Kaw) and considering two cases, large water volume (disinfection use in solution) and small water volume (disinfection use on surfaces), the partitioning of DBPs and biocidal a.s. during the biocidal use was calculated. A potential subsequent partitioning in a waste water treatment plant was modelled using calculated organic carbon - water distribution coefficients (Koc). The results of the modelling showed that a large proportion of DBPs behaved differently compared to the a.s.. The consequence is that most of the DBPs would not be covered by the ERA for the a.s..

Simulation experiments and genuine samples

For the experimental part of the project, 61 DBPs were chosen as target analytes. The choice of the DBPs selected for the analytical experiments was primarily based on the evaluation of the

literature search on DBPs and technical feasibility. Besides the frequency of occurrence in the evaluated literature, the selection also considered the broad spectrum of substances found in the literature.

The experimental part of the project consisted of two main parts, analysis of laboratory disinfection simulations and analysis of samples from genuine disinfection uses. The laboratory disinfection simulations were performed using two matrix compositions known from efficacy tests, one focusing on disinfection uses in swimming pools and one containing organic matter that can be generally expected for disinfection uses across the regarded PTs. Simulations were performed in aqueous solutions for both matrices. For the general matrix, additional simulations on surfaces were performed. All set-ups were tested using hypochlorite as biocidal a.s. and selected set-ups with hypobromite, hydrogen peroxide and chloramine T. Different reaction parameters (concentrations of matrix and a.s., temperature, pH and time) were varied to establish worst-case conditions for DBP formation. Samples from genuine disinfection uses encompassed samples from swimming pools, pools within a thermal spa and samples from cooling systems.

The analytical results of the laboratory simulations showed the complex system of reactions taking place after applying a.s. in presence of matrix and water. These reactions did not only consist of reactions of the a.s. with organic and inorganic matrix constituents but also included continuous reactions between the a.s., matrix and already formed DBPs. The system was too interconnected to define worst-case conditions, even in controlled laboratory experiments. Conditions leading to a high formation of a specific class of DBPs might at the same time lead to a decreased formation of another class changing the composition of the formed DBPs. The genuine samples from real disinfection processes underlined this finding. In reality, even more factors such as technical operations during water processing or other chemicals added to the water influenced the formation of DBPs. It was not possible to understand all processes influencing the DBP formation. The partially unexpected results indicated that unknown parameters with an influence on DBP formation might not have been controlled in the experiments. Furthermore, the project was limited to target analyses and thus to a reduced set of DBPs and their choice was influenced by the strong bias of the literature on chlorination as disinfection use. Therefore, especially for non-halogenating a.s. such as hydrogen peroxide the findings of the project were limited. Despite extensive experimental work, the project was not able to produce values that could be used as formation fraction for the calculation of PECs for DBPs that would be needed for a refined single substance assessment of DBPs.

Conclusions

Considering the results of the project, conclusions for the ERA of DBPs were developed. The existing guidance (ECHA, 2017) delivered a reasonable framework but it lacks detailed descriptions for the assessment procedure and does not regard all a.s. and PT at the moment. In order to ensure a consistent and manageable ERA process for DBPs several proposals were made:

- Definition of DBPs
- Criteria to rule out DBP formation
- Categories of active substances and assignment to their potential DBPs
- Criteria to choose DBPs for single substance assessment
- Implementation of an DBP factor

However, the proposed strategy is still incomplete and research need on several topics was identified. Insufficient data is available on possible DBPs generated by non-halogenating biocidal a.s.. This is especially important as such DBPs may have significantly differing properties compared to the DBPs discussed in the literature so far. No literature data with respect to DBP formation is available for biocidal uses on surfaces and the experiments in the present study can only be regarded as a starting point. Finally, if experimental studies are intended to be a part of ERA of DBPs, there is a general research need in order to define simulation conditions considering all relevant factors influencing DPB formation for the different disinfection uses. It remains unclear how to conduct these detailed analyses based on the complexity of the issue and many parameters influencing the reactions.

Zusammenfassung

Die Umweltrisikobewertung nach dem Vorsorgeprinzip ist ein zentrales Element der Verordnung für Biozidprodukte in der EU (EU, 2012; Biocidal Products Regulation, BPR). Desinfektionsmittel und Schutzmittel in industriellen Prozessen, der Gegenstand dieser Studie, gehören zu diesen Biozidprodukten, die von der BPR erfasst werden. Ihre Wirkungsweise umfasst unterschiedliche Prinzipien, darunter auch eine hohe chemische Reaktivität des jeweiligen bioziden Wirkstoffs. Mögliche Reaktionsprodukte, die während der Desinfektion entstehen, müssen ebenfalls bei der Umweltrisikobewertung des betreffenden bioziden Wirkstoffs oder bei Produktzulassungen berücksichtigt werden. Das generelle Vorgehen für die Umweltrisikobewertung dieser sogenannten Desinfektionsnebenprodukten (disinfection-by-products, DBPs) wird in der „Guidance on Disinfection By-Products“ (ECHA, 2017) beschrieben. Die Guidance hat jedoch noch Limitationen und es laufen derzeit Diskussionen, wie die Risikobewertung der DBP gestaltet werden soll. Darüber hinaus ist die Guidance auf halogenierte DBPs und die Produkttypen (PTs) 2, 11 und 12 beschränkt. Folglich wird derzeit keine harmonisierte wissenschaftlich fundierte Umweltrisikobewertung von DBPs durchgeführt, was die gegenseitigen Anerkennungen der Produktzulassung erschweren kann.

Das Ziel des vorliegenden Projekts war es, vorhandene Daten zu DBPs und bioziden Wirkstoffen aus relevanten PTs zusammenzutragen, die innerhalb der EU genehmigt sind oder sich im Genehmigungsverfahren befinden. Die PTs 1-5, 11 und 12 wurden als für das Projekt relevant identifiziert. In diesen PTs kommen die Wirkstoffe während der Desinfektionsanwendungen mit organischen Matrizes in Kontakt und die entstandenen DBPs können in die Umwelt gelangen und sind deshalb für die Umweltrisikobewertung relevant. Darüber hinaus war die Überprüfung der Relevanz der identifizierten DBPs für die Umweltrisikobewertung durch die Abschätzung potenzieller Eintragspfade in die Umwelt Teil des Projektes. Durch Analyse von Proben sowohl aus experimentellen Desinfektionssimulationen als auch aus realen Anwendungen wurden die theoretischen Schlussfolgerungen überprüft. Basierend auf den erzielten Ergebnissen wurden Änderungen und Ergänzungen für die Umweltrisikobewertung von DBPs vorgeschlagen.

Literaturrecherche zu DBPs

Die Literaturrecherche zu DBPs erfolgte im Zeitraum von 2013 bis April 2019 und umfasste auch ausgewählte Publikationen vor 2013, wenn in neuerer Literatur darauf verwiesen wurde. Aus knapp 3000 Suchergebnissen wurden 154 Publikationen durch Screening von Titeln und Abstracts als relevant ausgewählt. Durch die Auswertung der ausgewählten Literatur wurden 272 DBPs identifiziert, davon sind 186 halogenierte und 86 nicht-halogenierte DBP. Die detaillierten Ergebnisse der Literaturrecherche wurden in Excel-Tabellen mit DBP-Daten (Name, Molekülstruktur, Summenformel und CAS-Nr., Bildungsbedingungen, Name und CAS-Nr. des verwendeten Biozid-Wirkstoffs und der behandelten Matrix) zusammengestellt.

Im Hinblick auf die Ziele des Projekts war das Ergebnis der Literaturrecherche aufgrund mehrerer Spezifika, die für fast alle Studien galten, eingeschränkt. Eine wesentliche Einschränkung war der Fokus der Forschung auf nur sehr wenige hochreaktive Wirkmechanismen. Die untersuchten bioziden Substanzen wirkten zu ca. 90% durch Chlorierung und die restlichen ca. 10 % durch Oxidation. Folglich umfassen die Ergebnisse nur relativ kleine DBP, die typischerweise aus der Wirkung der hochreaktiven Wirkstoffe resultieren. Es wurden keine Informationen zu DBPs gefunden, die von anderen, weniger reaktiven bioziden Wirkstoffen, beispielsweise Carbonylverbindungen, erzeugt werden, obwohl eine DBP-Bildung im Allgemeinen auch für diese Stoffe realistisch ist. Darüber hinaus konzentrierte sich die Literatur offensichtlich nicht auf konkrete regulatorisch definierte biozide Wirkstoffe, sondern eher generell auf eine bestimmte Reaktivität der Wirkstoffe, wie

Chlorierung oder Oxidation. Folglich waren nur sehr begrenzte Informationen zum konkreten DBP-Bildungspotential von regulatorisch definierten bioziden Wirkstoffen verfügbar und eine direkte Zuordnung von DBP zu bestimmten bioziden Wirkstoffen war nicht möglich. Schließlich wurde keine Literatur gefunden, die eine DBP-Bildung bei der Desinfektion von Oberflächen behandelt. Die gesamte erfasste Literatur beschreibt nur Experimente in wässrigen Lösungen, dabei können in Abwesenheit von Wasser andere DBP erzeugt werden.

Die Bedingungen, unter denen DBP entstehen, sind stark von verschiedensten Faktoren abhängig, weshalb aus der Literatur keine allgemeingültigen Aussagen zum Bildungspotential getroffen werden konnten. Basierend auf den Ergebnissen der Literaturrecherche ließ sich kein genereller Trend für bestimmte DBP-Klassen oder einzelne Vertreter erkennen. Daher reichen die Ergebnisse der Literaturrecherche nicht aus, um Rückschlüsse darauf zu ziehen, welche speziellen DBP für eine Einzelstoffbewertung ausgewählt werden sollten, um trotzdem noch dem Vorsorgeprinzip folgen zu können.

DBP-Bildungspotential von bioziden Wirkstoffen

Eine Liste biozider Wirkstoffe, die innerhalb der EU genehmigt sind oder sich im Genehmigungsverfahren befinden (Stand Juli 2019), wurde unter Verwendung der ECHA-Datenbank erstellt. Die resultierende Liste umfasste 32 genehmigte biozide Wirkstoffe und 94 biozide Wirkstoffe innerhalb des Genehmigungsverfahrens. Es wurden grundlegende Daten zu den bioziden Wirkstoffen (Summenformel und Struktur, CAS-Nr, PT) und zusätzliche Informationen über das Potenzial zur Bildung von DBPs basierend auf Experteneinschätzung zusammengestellt.

Die bei der Verwendung biozider Wirkstoffe gebildeten Arten und Mengen von DBPs können jedoch nicht allgemein auf der Grundlage bestimmter Kategorien wie der PT abgeleitet werden, innerhalb derer ein Wirkstoff bewertet wird. Obwohl die organischen Substanzen in der bei der bioziden Anwendung vorliegenden Matrix innerhalb der betrachteten PTs im Allgemeinen vergleichbare Bestandteile haben wird, werden sich die Konzentration und die detaillierte Zusammensetzung der Matrix zwischen den PTs, aber auch zwischen bestimmten Anwendungen innerhalb derselben PT stark unterscheiden. Zusätzlich kann das Vorhandensein und die Menge von Wasser ein wichtiger Faktor für die DBP-Bildung sein und zu unterschiedlichen Reaktionen und einer Veränderung der generierten DBP führen.

Für die betrachteten bioziden Wirkstoffe wurden zwei Ansätze zur Kategorisierung hinsichtlich des DBP-Bildungspotentials entwickelt, einer nach der Wirkweise (mode of action) und einer nach der chemischen Struktur der bioziden Wirkstoffe. Die Kategorisierung gemäß der Wirkweise stellte sich im Detail als komplex heraus, während sich der zweite Ansatz als geeignet für das Projekt erwies. Als Ergebnis der Experteneinschätzung und der Kategorisierung ergab sich für 57 von 126 bioziden Wirkstoffen ein relevantes Potenzial für die Bildung von DBPs.

Die Klassen, in die die Wirkstoffe eingeordnet wurden, wurden dann den einzelnen DBPs zugeordnet, die in der Literatur gefunden wurden. Dieser Umweg über die Klassen war notwendig, da in der Literatur, wie oben beschrieben, selten konkrete Wirkstoffe in den Studien benannt wurden, sondern nur Reaktionstypen (z.B. Chlorierung oder Oxidation). Dank der Kategorisierung in Klassen können die erwarteten DBP für bestimmte biozide Wirkstoffe dennoch eingegrenzt werden.

Eintragspfade in die Umwelt

Unter der Annahme, dass ein Grund für eine separate Umweltrisikobewertung eines DBP ist, wenn sich seine Verteilung in den Umweltkompartimenten im Vergleich zu dem bioziden Wirkstoff unterscheidet, wurden mögliche Eintragspfade ausgewählter DBP und biozider

Wirkstoffe in die Umwelt mit einem Modellierungsansatz abgeschätzt. Die Modellierung konzentrierte sich hauptsächlich auf die Frage, ob die Verteilung für DBPs und biozide Wirkstoffe unterschiedlich ist oder nicht. Unter Verwendung berechneter Luft-Wasser-Verteilungskoeffizienten (Kaw) und unter Berücksichtigung von zwei Fällen, großem Wasservolumen (Desinfektionsanwendung in Lösung) und kleinem Wasservolumen (Desinfektionsanwendung auf Oberflächen), wurde die Verteilung von DBPs und bioziden Wirkstoffen während der Biozidanwendung berechnet. Eine mögliche nachträgliche Verteilung in einer Kläranlage wurde mit berechneten organischen Kohlenstoff-Wasser-Verteilungskoeffizienten (Koc) modelliert. Die Ergebnisse der Modellierung zeigten, dass sich ein Großteil der DBPs anders verhielt als der Wirkstoff. Die Folge wäre, dass die meisten DBPs nicht von der Umweltrisikobewertung für den Wirkstoff abgedeckt wären.

Simulationen und reale Proben

Für den experimentellen Teil des Projekts wurden 61 DBPs als Analyte ausgewählt. Die Auswahl der für die analytischen Experimente ausgewählten DBPs basierte in erster Linie auf der Auswertung der Literaturrecherche zu den DBPs und den technischen Möglichkeiten. Bei der Auswahl wurde neben der Häufigkeit der Nennung in der ausgewerteten Literatur auch das breite Spektrum der in der Literatur gefundenen Substanzen berücksichtigt.

Der experimentelle Teil des Projekts bestand aus zwei Hauptteilen, der Analyse von experimentellen Desinfektionssimulationen und der Analyse von Proben aus realen Desinfektionsanwendungen. Die experimentellen Desinfektionssimulationen wurden mit zwei Matrices durchgeführt, von denen eine Desinfektionsanwendungen in Schwimmbädern abbildete und eine weitere, die organische Bestandteile enthielt, die allgemein für Desinfektionsanwendungen in den betrachteten PTs erwartet werden kann. Die Simulationen wurden in wässrigen Lösungen für beide Matrices und zusätzlich an Oberflächen für die allgemeine Matrix durchgeführt. Alle Ansätze wurden mit Hypochlorit als bioziden Wirkstoff durchgeführt und ausgewählte Ansätze zusätzlich mit Hypobromit, Wasserstoffperoxid und Chloramin T. Verschiedene Reaktionsparameter (Konzentrationen von Matrix und Wirkstoff, Temperatur, pH-Wert und Zeit) wurden variiert, um Worst-Case-Bedingungen für die DBP-Bildung abzuschätzen. Proben aus realen Biozidanwendungen umfassten Proben aus Schwimmbädern, Becken eines Thermalbades und Proben aus Kühlsystemen.

Die analytischen Ergebnisse der Laborsimulationen zeigten ein komplexes Reaktionssystem nach Anwendung von bioziden Wirkstoffen in Anwesenheit von Matrix und Wasser. Neben Reaktionen der Wirkstoffe mit organischen und anorganischen Matrixbestandteilen fanden weitere Reaktionen zwischen dem Wirkstoff, der Matrix und bereits gebildeten DBPs statt. Das System war zu komplex, um Worst-Case-Bedingungen selbst unter kontrollierten Laborexperimenten zu definieren. Reaktionsbedingungen, die zu einer hohen Bildung einer bestimmten Klasse von DBPs führen, können gleichzeitig zu geringeren Bildung einer anderen Klasse von DBPs führen, wodurch sich die Zusammensetzung der gebildeten DBPs ändert. Die Proben aus realen Desinfektionsanwendungen unterstrichen diesen Befund. Tatsächlich beeinflussten noch weitere Faktoren wie technische Vorgänge bei der Wasseraufbereitung oder andere dem Wasser zugesetzte Chemikalien die Bildung von DBPs. Es war nicht möglich, alle Prozesse zu verstehen, die die DBP-Bildung beeinflussen. Die teilweise unerwarteten Ergebnisse deuteten darauf hin, dass unbekannte Parameter mit Einfluss auf die DBP-Bildung in den Experimenten möglicherweise nicht kontrolliert wurden. Darüber hinaus war das Projekt auf die Analyse definierter DBP („Taget"-Analyse) und damit auf eine reduzierte Anzahl von DBPs beschränkt, und ihre Auswahl wurde durch die starke Ausrichtung der Literatur auf Chlorierung als Desinfektionsanwendung beeinflusst. Daher sind insbesondere für nicht-halogenierende Wirkstoffe wie Wasserstoffperoxid die Ergebnisse des Projekts eingeschränkt aussagekräftig.

Trotz umfangreicher experimenteller Arbeiten konnte das Projekt keine Werte liefern, die als Bildungsfraktion für die Berechnung von PECs für DBPs verwendet werden könnten, die für eine verfeinerte Einzelstoffbewertung von DBPs benötigt würden.

Schlussfolgerungen

Unter Berücksichtigung der Ergebnisse des Projekts wurden mögliche Optionen für die Umweltrisikobewertung von DBPs entwickelt. Die bestehende Richtlinie (ECHA, 2017) liefert einen sinnvollen Rahmen, aber es fehlen detaillierte Beschreibungen für das Bewertungsverfahren. Zudem werden nicht alle relevanten Wirkstoffe und PTs erfasst. Zur Gewährleistung eines einheitlichen und überschaubaren Prozesses der Umweltrisikobewertung von DBPs wurde folgende Vorschläge erarbeitet:

- DBP-Definition
- Kriterien für den Ausschluss einer DBP-Bildung durch biozide Wirkstoffe
- Kategorien von Wirkstoffen und Zuordnung zu ihren potentiellen DBPs
- Kriterien für die Relevanz von DBPs für Einzelstoffbewertungen
- Einführung eines DBP-Faktors

Die vorgeschlagene Strategie ist jedoch weiterhin unvollständig, und es wurde weiterer Forschungsbedarf zu mehreren Themen identifiziert. Es liegen nur unzureichende Daten zu möglichen DBPs vor, die durch nicht-halogenierende biozide Wirkstoffe generiert werden. Dies ist besonders wichtig, da solche DBPs deutlich unterschiedliche Eigenschaften im Vergleich zu den bisher in der Literatur diskutierten DBPs haben können. Für biozide Anwendungen auf Oberflächen liegen keine Literaturdaten bezüglich DBP-Bildung vor und die Experimente in der vorliegenden Studie können nur als Ausgangspunkt betrachtet werden. Schließlich, falls experimentelle Studien Teil der Umweltrisikobewertung von DBPs sein sollen, besteht ein allgemeiner Forschungsbedarf, um Simulationsbedingungen unter Berücksichtigung aller relevanten Faktoren für die DBP-Bildung bei verschiedenen Desinfektionsanwendungen zu definieren. Es bleibt noch unklar, wie derartigen Untersuchungen angesichts der Komplexität und der Vielzahl an Parametern, die die Reaktionen beeinflussen, durchgeführt werden können.

1 Introduction

"Regulation (EU) No 528/2012 of the European Parliament and the Council of 22 May 2012 concerning the making available on the market and use of biocidal products" (EU, 2012; Biocidal Products Regulation, BPR) is based on the precautionary principle. The aim of the Regulation is the identification, evaluation and prevention or at least decrease of adverse effects and risks on humans and environment caused by the manufacturing and use of biocidal active substances and products. An essential element for this approach is the environmental risk assessment (ERA). For this assessment, information about the substance toxicity, its release pathways, its fate and behaviour in the environment as well as the resulting environmental concentrations is required.

The biocidal products, as well as, their residues are considered particularly in the BPR in Article 19 (1) (iii). In this context, the term residue refers to a substance, which is present "in or on products of plant or animal origin, water resources, drinking water, food, feed or elsewhere in the environment and resulting from the use of a biocidal product, including such a substance's metabolites, breakdown or reaction products." (Article 3 (1) (h)).

When using disinfectants and preservatives, which are the topic of this study, various by-products (disinfection by-products, DBPs) are formed due to the high reactivity of the active substances contained in the used biocidal products. Therefore, these reaction by-products also need to be considered for risk assessment. This represents a major challenge, due to fact that the identity and the amount of formed by-products are depending on the application conditions, the release pathways into environment and the environmental conditions in the primary compartment (optionally also in the secondary compartment). Therefore, the prediction of the identity and environmental concentration of the by-products, as an important part of the risk assessment, is difficult.

In literature, several references confirm the formation of DBPs by different uses. However, the number of identified DBPs is very high in most cases (partially more than 500 DBPs) and there is little knowledge of their properties. Therefore, besides a few exceptions, no general statement for the necessity of a single substance environmental risk assessment for DBPs can be made.

An existing European Guideline on the assessment of DBPs in the biocides authorisation process (ECHA, 2017) is only focussing on the use of halogenated substances, as well as on the biocidal product type (PT) 2 (disinfectants and algaecides, not intended for direct application to human or animals), 11 (preservatives for liquid-cooling and processing systems) and 12 (slimicides). As this existing guidance is relatively abstract, a detailed instruction manual for the implementation of an environmental risk assessment of DBPs is still missing. Therefore, information and data submitted by applicants on the formation of DPBs for a respective biocidal active substance or biocidal product can be interpreted in different ways by individual EU member states and a harmonized environmental risk assessment of DBPs might not be conducted. Finding individual solutions for this problem binds important capacities of the member states and delays the assessment process. Furthermore, the consideration of the precautionary principle and the level of protection in the EU member states may be different. This might hamper mutual recognitions of product authorisations between member states.

The goal of this study was to develop a strategy how to assess DBP best during the environmental risk assessment. As basis for the strategy, the existing knowledge on DBPs and their formation potential under different circumstances was evaluated (chapter 2), biocidal active substances were rated regarding their DBP formation potential (chapter 3) and the potential entry routes of DBP were analysed (chapter 5). The theoretical results were then

validated against laboratory and field experiments on DBP formation in different matrices (chapter 6). The last chapter contains options for a protective and pragmatic approach how to consider DBPs best during the environmental risk assessment of biocidal active substances and products (chapter 7).

2 Literature research on DBPs

2.1 Definition of DPBs

DBPs can be defined in different ways, resulting in different types and numbers of substances to be considered. The application of a biocidal active substance will always occur in presence of a matrix. The matrix may consist of organic and/or inorganic matter, differ in wide range with respect to the composition and also with respect to its physical state like solid, liquid or dissolved matter. Within the present project, **DBPs are defined as reaction products of the biocidal active substance with the matrix present during the application of the biocidal product.** Consequently, this definition excludes for example environmental degradation products, as these would be generated subsequent to the application of the biocidal product. In some cases, the reactive molecule is released from a biocidal active substance forming a not active by-product at the same time. These reaction by-products are also not covered by the aforementioned definition of DBPs agreed for this project.

2.2 Methods

To answer the abovementioned questions, a systematic literature research was performed using the search-terms „disinfection by-product*“ OR „disinfection by product*“ in the database Web of Science. Our search resulted in 2928 entries for the years 2013 to April 2019. Newer publications after April 2019 were not included in this literature search. As the use of disinfectants experienced a significant increase due to the pandemic afterwards, it can be assumed that the number of publications on this topic increased even further. From these results, 154 relevant publications (including selected publications before 2013 through references in newer literature) were selected via expert judgement (screening of titles and abstracts).

To test whether the chosen search terms were adequate, exemplary searches with alternatives were conducted to see if relevant publications would still be found and that comparable results would be achieved. Alternative search terms were „by-product“ or „transformation product“. As relevant publication for non-halogenated DBPs, Walse and Mitch, 2008 with 24 different DBP/substance combinations was chosen. Examples for alternative search terms are listed in Table 1 for publications in the year 2008. As can be seen from Table 1 “disinfection by-product” is the adequate search term that is not too broad and does not unduly limit the results.

Table 1: Results of the literature research on disinfection by-products using different search terms

search term	results	concordance	contains Walse and Mitch
disinfection by-product	211	211	yes
by-product	2328	211	yes
by-product + chlorine	2328	62	yes
transformation product	1979	10	no
transformation product + disinfection	12	10	no

2.3 Results

After evaluating the 154 identified publications, 272 DBPs were found in total. Based on these data, DBPs were divided into two groups: i) of halogenated and ii) non-halogenated DBPs and were further subdivided as stated in the following list. The list contains all DBP groups and the

number of the therein contained substances as well as the number of appearances in literature sources.

Halogenated DBP (186 substances, 882 appearances):

- Trihalomethanes (THMs) (13 substances, 226 appearances)
- Other Haloalkanes (2, 3)
- Haloacetic Acids (HAAs) (13, 59)
- Other Haloacids (13, 23)
- Halodiacids (9, 13)
- Haloacetonitriles (HANs) (8, 121)
- Haloacetamides (HAcAms) (14, 42)
- Halonitromethanes (HNMs) (8, 27)
- Haloketones (HKs) (12, 51)
- Haloaldehydes (10, 43)
- Haloamines (4, 13)
- Halobenzoquinones (6, 17)
- Inorganic ions (9, 21)
- Halogenated fatty amides (7, 7)
- Dihalo-4-hydroxybenzaldehydes (3, 3)
- Dihalo-4-hydroxybenzoic acids (3, 3)
- Dihalo salicylcic acids (3, 3)
- Trihalo-phenols (6, 7)
- Other (43, 67)

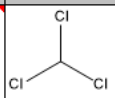
Non-halogenated DBP (86 substances, 299 appearances):

- N-Nitrosamines (11, 80)
- Carboxylic acids (25, 59)
- Other (60, 152)

An overview of the DPBs included in the tables can be found in annex A. The detailed results of the literature review were compiled in an Excel sheet, which can be downloaded as an annex to this report on the homepage of the Environment Agency (https://www.umweltbundesamt.de/publikationen, name of the document: “FKZ 3718 65 403 0_Excel annex to DBP project“, spreadsheets “DBP_Halogenated DBPs” and “DBP_Non-halogenated DBPs”). The sheets include DBP data (name, molecular structure, molecular formula

and CAS No), formation conditions (name and CAS No of applied active substance and treated matrix) and references (literature reference and alignment with GESAMP-BWWG-list).

Figure 1: Structure of the table containing the detailed results of the literature search on DBPs

DBP	Structure Formula	Molecular Formula	CAS	Applied active substance	CAS2	Treated matrix	Literature source	Considered by GESAMP-BWWG
Trihalomethanes (THMs)	Trihalomethanes (THMs)							
trichloromethane		CHCl3	67-66-3	hypochlorite	14380-61-1	indoor swimming pool	Aprea et al., 2010	Y

Source: own illustration, structure of Excel table summarising literature searach on DBPs.

2.3.1 Influencing factors on the formation of DBPs depending on use area

The results of the literature review show that a large part of the findings belongs to disinfection by-products that are already regulated in some directives or norms that have been implemented in certain countries for specific uses. These include trihalomethanes (THM), haloacetic acids (HAA) as well as individual representatives from the haloacteonitriles (HAN) and nitrosamines. Trihalomethanes (THM), comprising trichloromethane (chloroform), bromodichloromethane, dibromochloromethane and tribromomethane (bromoform), are often regulated together. Haloacetic acids (HAA) include monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA). N-nitrodimethylamine (NDMA) from the group of nitrosamines also belongs to the regulated disinfection by-products.

Trihalomethanes, haloacetic acids and nitrosamines (NA) are often registered by regulations as disinfection by-products in drinking or swimming pool water (Richardson, Plewa, Wagner, Schoeny, & DeMarini, 2007). The conditions under which these disinfection by-products are formed are strongly dependent on the active substance concentration, the temperature (Kanan & Karanfil, 2011), the pH value (Hansen, Albrechtsen, & Andersen, 2013) and the total organic carbon (TOC) present in the water, which is why no general statements on their formation potential in this use area can be made here.

For other areas of application such as soil disinfection or the food industry, no regulated disinfection by-products besides chlorite and chlorate are known (EU- Commission Regulation (2020)). Those are also known disinfection by-products in other non-aqueous applications and often find their way into products through washing steps with water containing biocides. It was shown that in the area of the regulated DBP classes in aqueous applications comprising haloacetic acids, trihalomethanes and nitrosamines, certain environmental conditions can have an influence on the formation of these DBP classes. Haloacetic acids are preferentially formed more at lower pH values, whereas trihalomethanes are predominantly formed under higher pH conditions (Hung et al., 2017). Increased DBP formation was also observed with increasing temperature (Hansen et al., 2013), that at the same time accelerates the decomposition of some DBP classes into others, such as the haloacetic acids into the trihalomethanes. It must be mentioned that in the case of volatile DBP classes (e.g. trihalomethanes), a significant part volatilises due to the high vapour pressure (Lourencetti et al., 2010). Nitrosamines are preferentially produced by chloramination (oxidation of NOM) or reaction with nitrogenous precursors (e.g. dimethyl-amines) (Piazzoli, Breider, Aquillon, Antonelli, & von Gunten, 2018). Many studies have shown that with increasing matrix load, more DBP formation takes place.

However, no proportional dependence of TOC with regulated or frequently investigated DBP classes is recognizable here, since a large part of the halogenated organic carbon (AOX) formed has not yet been investigated.

Regarding DBP classes not yet regulated, several investigations have already been carried out, but the values vary significantly depending on the matrix being investigated. This is in line with the results of this study presented in chapter 6.

2.3.2 Formation potential of specific DBP classes

Based on the results of the literature search, there is no general trend for certain DBP classes or individual representatives. It is obvious that some regulated classes such as THMs, HAAs, NAs are investigated more frequently due to existing regulations and thus have been found more often in studies, but this by no means implies at the same time that other substances of unregulated DBP classes are not formed. Other findings in literature are based on certain precursor substances that occur in artificial laboratory simulations (e.g., chlorination of UV filters (Manasfi, Coulomb, & Boudenne, 2017)) or only in certain matrices (bromide-rich baths, chlorination of peptide solutions/algae). The extent to which DBPs found in such laboratory studies occur in reality and how relevant they are regarding environmental risk assessment is not yet known.

2.3.3 Relevance of the GESAMP-BWWG list for estimating DBP formation

In total, the GESAMP-BWWG list contains 42 substances, 32 of which were also found in our DBP literature review. 240 DBPs were found in our literature search that are not included in the GESAMP-BWWG list. The GESAMP BWWG list and the DBP list established in the present study show a high similarity in the already regulated DBP classes trihalomethanes (THM), haloacetic acids (HAA) as well as haloacetonitriles (HAN). Other representatives such as inorganic DBPs like bromate or haloalkanes other than THMs are also represented in the GESAMP BWWG list. The DBP list of the present study comprises more representatives for the individual DBP classes than the GESAMP-BWWG list. Of the 42 substances in the GESAMP-BWWG list, only two are non-halogenated, which belong to the class of aldehydes. Substances from the class of carboxylic acids or nitrosamines or other non-halogenated DBPs are not included in the GESAMP-BWWG list and only occur in the DBP list of the present study. Furthermore, the GESAMP BWWG list does not include any iodine-containing DBPs, which could be due to the fact that these were not studied at the time the GESAM BWWG list was compiled and have only found their way into the literature in recent years (Dong et al., 2019). Iodinated DBPs are considered to be much more toxic than their brominated and chlorinated analogues (Postigo et al., 2018). It thus appears that the GESAMP-BWGG list should be revised both with regard to the assessment of ballast water treatments and for a general update to include new DBP classes. For biocidal applications in aqueous systems, the GESAMP BWWG list could be taken as a basis for preliminary screening, but would need to be supplemented by additional important commonly occurring DBPs such as the nitrosamines. A general transfer of the list for application in biocide areas is not recommended, as in non-aqueous systems other DBP classes e.g. chlorinated peptides might dominate the generated DBPs and the distribution of DBPs might differ (see below).

2.3.4 Formation of DBPs in non-aqueous systems and applications

In the food industry, washing water is often used to kill microorganisms or to prevent contamination within the production of food. The storage of food in biocide-containing water is also an important method for reducing the growth of harmful microorganisms. Cardador et al. were able to show in several studies on various foods such as fruit juices, soft drinks, cheese and

frozen vegetables that their treatment with biocides or with biocide-contaminated water can also lead to the formation of DBPs (Cardador et al., 2016; Cardador et al., 2017). Often, these studies only examine regulated DBP classes such as the haloacetic acids or trihalomethanes. Non-regulated DBPs could only be detected in isolated studies. Bao et al were able to detect 3-chlorotyrosines as DBPs in the treatment of vegetables with hypochlorite solution (Bao Loan et al., 2016). Lee et al were able to detect other DBP classes such as haloketones (HKs) and aldehydes in addition to THMs and HAAs in lettuce wash water. However, in all mentioned publications the DBP formation takes place in presence of water, therefore studies on the application of biocides in non-aqueous systems are necessary to be able to make comprehensive recommendations on the assessment of these applications. Non-aqueous systems like surface disinfection were not found in the DBP literature review of the present study. They are either not relevant or until now not investigated for some reason such as difficult methodology. Another aim of these studies should be the screening for unknown DBPs, as it has already been shown in laboratory studies on aqueous solutions of amino acids that unknown and thus unregulated DBPs are formed (Richardson et al., 2019).

2.3.5 Limitations of literature search on DBP

The original plan of the present project was to obtain comprehensive information on DBP formation by the literature search on DBPs. As part of this information, a list of biocidal active substances was planned to be developed, with all active substances experimentally proven to form DBPs. This list was supposed to influence the evaluation of the literature search on biocides (chapter 3) and the choice of potentially DPB forming biocidal a.s. for the laboratory experiments (chapter 4). However, despite the extensive literature search on DBPs, the outcome with respect to the targets of the project was only limited due to several specific characteristics of almost all literature on DBPs.

A main limitation of the available literature is the focus on only very few highly reactive molecules. In approx. 90% of the searched literature on DBPs, chlorination is being investigated. As biocidal a.s., chlorine, hypochlorite and chloramine are used. The remaining 10% of the searched literature on DBPs deals with biocidal a.s. acting by oxidation like peroxides, ozone and chlorine dioxide. Even another highly reactive molecule like bromine, the reactive molecule in numerous biocidal a.s. being within the approval process, is represented only by two references. The biocidal a.s. acting by carbonyl reactivity are not present in the literature on DBPs at all. Consequently, the literature search on DPB delivers only very limited information about potentially DPB forming biocidal a.s., besides the ones which are quite obvious.

Only in exceptional cases the experiments described in the literature are referencing to a specific biocidal a.s. as approved or being within the approval process. The information on the chlorine sources applied in the described experiments are mostly limited to chlorination and hypochlorite. Further mentioned chlorine sources are di- and trichloroisocyanuric acid (troclosene) and bromo-chloro-dimethylhidantoin (BCDMH), while 8 different chlorinating biocidal active substance (only chlorinating activity) are under regulatory assessment. Similar results are observed for the biocidal active substance with a peroxide moiety. In the references, hydrogen peroxide, peracetic acid and persulfate are used as reactive molecule. In contrast, 11 biocidal a.s. base on peroxo-compounds are assessed under the BPR. The experimental work described in the literature obviously focuses on a particular reactivity like chlorination or oxidation and is mostly not considering regulatory defined biocidal a.s.. As a consequence, only little information allows a comparison of the DPB forming potential between the different biocidal active substances with the same reactive molecule. Furthermore, the possibilities to link the results of the literature search on DBP to specific biocidal a.s. with DBP formation potential

are limited. Often, only a link to a whole group of biocidal active substance having the same reactive molecule is possible and reasonable. To be anyway able to link the results of the literature search to biocidal active substances under the BPR, a categorisation of the a.s. was used. More details can be found in chapter 3.2.

Finally, no references focusing on DBP formation during disinfection of surfaces were found. All searched literature describes experiments in aqueous solutions. Therefore, no information was available about amounts of DBPs formed during surfaces uses and especially whether significant differences to uses in solutions are observed. Besides the amount of DBP, such differences may comprise the identity of the formed DBPs or the source of the DBPs with respect to the applied biocidal a.s.. As mentioned in chapter 2.3.4, the reaction conditions during surface disinfection may have an influence on the DBP formation, for example because water is present only in limited amounts. However, after the literature search this can only be assumed and no distinct impact referring to this is given for the evaluation of the literature search and the subsequent project progression.

2.4 Preliminary conclusions

The conditions under which disinfection by-products are formed are strongly dependent on a large variety of factors, which is why no general statements on their formation potential can be drawn from literature. Many studies have shown that with increasing matrix load, more DBP formation can take place. However, no proportional dependence of TOC with regulated or frequently investigated DBP classes has been recognized, since a large part of the halogenated organic carbon (AOX) formed has not yet been investigated in studies. To close this gap, non-target analysis would need to be deployed for all use areas.

Based on the results of the literature search, there is no general trend for certain DBP classes or individual representatives. For biocidal applications in aqueous systems, the GESAMP BWWG list could be taken as a basis for preliminary screening, but would need to be supplemented by additional important commonly occurring DBPs such as the nitrosamines.

To this point, the results of the literature search are not sufficient to draw conclusions on specific DBPs that would suffice to be considered during the assessment of specific use conditions whose solitary assessment would follow the precautionary principle.

3 Evaluation of DBP forming potential of biocidal active substances

3.1 Approach

The present project focuses on product types where active substances come in contact with organic matrices and potentially form DBPs. This reduces the number of relevant biocidal uses, which can serve as source for the relevant DBPs. In detail, biocidal active substances belonging to the main group 1 (PT 1 - 5) and PTs 11 and 12 from main group 2 were considered in the literature search.

In a first step, a list of biocidal active substances (a.s.) was compiled, which are either approved within the EU or within the approval process (status in July 2019). For this compilation the respective ECHA database (ECHA database, List of biocidal active substances) was used. The substance names, as listed in the ECHA database were amended by common names or acronyms. The resulting list of biocidal a.s. was supplemented with basic information on the substances including the CAS-number, the relevant PTs, a molecular formula and a molecular structure, if appropriate. For biocidal a.s. formed in situ information for the formed a.s. were given and for reaction mixtures no molecular formula and a molecular structure were given. Subsequently, the biocidal a.s. were evaluated whether they are in principle capable to generate DBPs during application due to their reactivity.

All relevant information of the evaluation for the biocidal active substances is summarised in Annex B. In the column “Status”, the table contains information about the approval status of the substance. Status “1” signifies that an active substance is approved (32 a.s.), status “2” means the initial approval is in progress (94 a.s.). The information was obtained from the ECHA database (main group 1 and 2, PT 1-5, 11, 12; status in July 2019). In addition to basic data about the biocides (e.g., molecular formula, CAS-No, product type (PT)) additional information about potential for the formation of DBPs is shown. This is based on expert judgement during the course of this study and is characterised by the categorisation as introduced in the following chapter.

3.2 Categorisation of the a.s. depending on DBP formation potential

As described in chapter 2.3.5, the literature data did often not specify exactly which regulatory defined biocidal a.s. was used to generate the DBP analysed in the experiments. For this reason, it was not possible within the project to directly link the biocidal a.s. to the DBPs from literature. To be nevertheless able to specify which DBP might result from the use of a biocidal a.s., a categorisation system was developed that categorized the biocidal a.s. in a system that suited the results from literature.

Two different approaches to classify the a.s. regarding their potential to form DBPs were developed. The first one followed a categorisation system according to the modes of action of the active substances. The second one categorised the a.s. according to their chemical structures. As the second approach proved to be more suitable for the project, it was used for the further discussion and interlinkage between a.s. and their potential DBP found in literature (chapter 2). Both approaches are described in the following two chapters.

3.2.1 Categorisation by “Mode of Action” (MoA)

The listed biocidal a.s. were categorised by their “Mode of Action” (MoA). Every biocidal active substance was assigned at least to one of the groups summarized in Table 2. If appropriate, a

substance was put into more than one group. The attribution of the modes of action for each a.s. can be found in Annex B. If possible, details specifying the MoA were added in brackets in that table.

Table 2: Categorisation of the biocidal active substances according to the "Mode of Action"

Mode of action	Details of the mode of action (if applicable)
Systemic	isothiazolone / cellular membrane, surface activity / polyamine / quarternary ammonium / enzyme inhibitor / MITC release / silver
Active carbonyl	formaldehyde release
Halogen	chlorination / bromination / iodination
Alcohol	
Acid	
Base	
Oxidation	peroxide
General chemical reactivity	
Chloramine	chlorination

The MoA classes were created following a pragmatic approach fulfilling the requirements of the present project. They should allow to assign the biocidal a.s. to a manageable number of MoA classes which can be correlated to a DBP formation potential.

The **systemic** MoA integrates the biggest number of structurally different biocidal active substances. They act quite differently for example by disturbing cellular membranes or inhibiting crucial enzymes. Therefore, for this MoA class the most details on information on the modes are assigned, if available. Almost all of them have a modest or low chemical reactivity in common. Consequently, their potential to form DBPs will be rather low.

In most cases, a reactive molecule (e.g. chloramine), a molecule family (e.g. halogen) or a chemical moiety (e.g. alcohol) is decisive for the biocidal activity. As the resulting MoA classes allow at the same time a conclusion on the DBP formation potential, it was reasonable to group the biocidal active substances according to these groups. **Alcohols**, **acids** and **bases** are significantly affecting biological activity and are suitable as biocidal active substances, but their chemical reactivity is modest and their potential to form DBPs will be low.

The biocidal activity of substances in the MoA classes **halogen**, **chloramine** and **oxidation** arises from their unspecific high chemical reactivity. Although in detail the reactivity as biocidal a.s. will differ depending on the single substance as well as on the particular biocidal use, the general DBP formation potential of those classes is high. For a.s. acting by halogenation and oxidation, the DBP formation is confirmed by literature references identified within the literature search on DBPs (chapter 2), with exception of a.s. with iodine as reactive molecule due to the lack of data.

A couple of biocidal active substances including formaldehyde, are active by their active **carbonyl** moiety. The DBP formation potential of the substances in this MoA class is complicated to judge. Generally, active carbonyl compounds have the potential to react with matrix components as present during the regarded biocidal uses. Main components of the matrices will be biomolecules or their breakdown products, comprising typical reaction partners for

carbonyls like amines. The carbonyl reactivity is responsible for the biocidal effects therefore respective reactions are obviously occurring. However, the chemical reactivity of the active carbonyls is less high and much more selective compared to halogens or oxidizing biocides. Furthermore, presence of water, to some extent given for the most of the regarded uses, reduces the typical carbonyl reactivity. Additionally, it is assumed that the resulting DBPs will still mostly have the character of the original matrix compounds. A variety of small molecules, generated though repeated reaction with the biocidal active substance is not expected. Therefore, the active carbonyls were assigned to have a moderate DBP formation potential.

Three biocidal active substances were assigned to the MoA class **general chemical reactivity**: bromoacetic acid, cyanamide and sulphur dioxide. They comprise generally a sufficient chemical reactivity to possibly form DBPs but no references on DBP formation in literature were found. Bromoacetic acid is, besides the acidic properties, an alkylating agent (Dondiano at al., 1986) and was therefore identified to possibly generate DPBs. For the resulting DBPs similar consideration as for the a.s. comprising an activated carbonyl function can be made. They will generally keep the main structure and characteristic of the matrix. Cyanamide comprises a moderate chemical reactivity and will also possibly react with the matrix present. In this case also the specific use may promote DBP formation. Cyanamide is mainly used for disinfection of piggeries. After application it is flushed into the manure tanks, therefore possible DBP formation is not limited by possible reaction partner or the reaction time. Finally, also the reactivity of sulphur dioxide was assessed as sufficient for reaction with surrounding matrix.

To classify the a.s. according to their mode of action provided some overview of the groups that might play a role. However, as the categorisation approach according to the chemical structure seemed more suitable to link a.s. and DBPs, this approach was further considered during the project.

3.2.2 Categorisation by chemical structure

Another possibility to classify the regarded biocidal active substances is the categorisation by the chemical structure responsible for the biocidal activity, as shown in Table 3. This approach leads to a clearer assignment of the most biocidal a.s. into a particular group, due to the distinct selection criterion. Although the chemical structure in the most cases also defines the mode of action of a biocidal active substance and the categorisation according to MoA and the chemical structure are similar, the results are not completely redundant.

For the categorisation by chemical structure the biocidal a.s. were first divided into two main groups: halogenated (class 1) and non-halogenated substances (class 2). Halogenated substances were further assigned into 5 groups represented by the corresponding reactive molecule, the numbering in the tables is accordingly. Where appropriate a sub- categorisation into organic, inorganic and in-situ representatives of a reactive molecule was performed. The group of chlorine dioxide shows that also the categorisation by chemical structure contains compromises. Although chlorinated and with respect to the reactivity mainly affected by presence of chlorine, chlorine dioxide primary reacts as an oxidising agent. Chlorination, typical for the other members of the a.s. group of halogens, only occurs under selected reaction conditions. It was therefore sorted to an own group. Due to the high reactivity, the halogenated biocidal active substances have a high potential of DBP formation.

The second main group of non-halogenated a.s. is much more diverse, with respect to the included chemical structures responsible for the biocidal activity. Included are the highly reactive oxidising substances like ozone and peroxides but also further seven groups relating to distinct chemical structure-element of the members responsible for the biocidal reactivity. In the last group, called “others” all the a.s. not fitting into any other of the groups are included. The

DBP formation potential of the non-halogenated a.i. differs depending on the reactive molecule. It is estimated to be fairly high for ozone and peroxides and moderate to low for the other groups of non-halogenated a.s.. The biocidal activity of some a.s., for example BCDMH, is based on more than one chemical structure. In this case, the a.s. was assigned to more than one group.

In order to estimate the relevance of the each a.s. group the number of PTs for which the respective a.s. are approved or are within the approval process in the EU was summed up in the column "No. of approval processes".

Table 3: Categorisation of the biocidal active substances by chemical structure

Class	Reactive molecules/moieties	Sub-groups	Represented biocidal active substances	No. of approval processes
1	Halogenated a.s.			
1.1	Hypochlorite			
1.1.1		Organic	Chloramin B (127-52-6), Tosylchloramide sodium (Chloramin T, 127-65-1), Symclosene (87-90-1), Sodium dichloroisocyanurate dihydrate (51580-86-0), BCDMH (32718-18-6), BCMEH (89415-87-2)	20
1.1.2		In-organic	Calcium hypochlorite (7778-54-3), sodium hypochlorite (7681-52-9), Chlorine (7782-50-5)	11
1.1.3		In-situ	Active chlorine (7782-50-5) from electrolysis, different sources	7
1.2	Hypobromite			
1.2.1		Organic	BCDMH (32718-18-6), BCMEH (89415-87-2), DBNPA (10222-01-2)	6
1.2.2		In-situ	Bromine (7726-95-6) from bromine chloride or sodium bromide with hypochlorite or ozone or chlorine or electrolysis	14
1.3	Iodine		Polyvinylpyrrolidone iodine (25655-41-8), Iodine (7553-56-2)	6
1.4	Monochloramine		Monochloramine (10599-90-3) varoius from ammonium carbamate, ammonium chloride, ammonium hydroxide, ammonia with chlorine source	7
1.5	Chlordioxide		Chlorine dioxide (10049-04-4) generated from sodium chlorite by electrolysis or the presence of sodium chlorate and hydrogen peroxide and strong acid or sodium chlorite and sodium bisulfate or sodium chlorite by acidification or sodium persulfate by acidification or sodium chlorite by oxidation, Chlorine dioxide generated from Tetrachlorodecaoxide complex (TCDO, 92047-76-2) by acidification	33

Class	Reactive molecules/moieties	Sub-groups	Represented biocidal active substances	No. of approval processes
2	Non-halogenated a.s.			
2.1	Ozone		Ozone (10028-15-6) generated from oxygen	4
2.2	Peroxide		Hydrogen peroxide (7722-84-1), MMPP (84665-66-7), 6-(phthalimido)peroxyhexanoic acid (PAP) (128275-31-0), Peracetic acid (79-21-0), Peroxyoctanoic acid (33734-57-5), Disodium peroxodisulphate/Sodium persulphate (7775-27-1), Peracetic acid (79-21-0) generated by perhydrolysis of N-acetylcaprolactam by hydrogen peroxide in alkaline conditions, Peracetic acid (79-21-0) generated from 1,3-diacetyloxypropan-2-yl acetate and hydrogen peroxide, Peracetic acid (79-21-0) generated from tetra-acetylethylenediamine (TAED) and sodium percarbonate, Performic acid (107-32-4) generated from formic acid and hydrogen peroxide, Pentapotassium bis(peroxymonosulphate) bis(sulphate) (70693-62-8)	34
2.3	Aldehydes			
2.3.1		Organic	Glutaral (Glutaraldehyde) (111-30-8), Glyoxal (107-22-2), Acrolein (107-02-8), Formaldehyde (50-00-0), Cinnamaldehyde (104-55-2)	12
2.3.2		In-situ	α,α',α''-trimethyl-1,3,5-triazine-1,3,5(2H,4H,6H)-triethanol (25254-50-6), HHT (4719-04-4),MBO (66204-44-2), TMAD (5395-50-6), Methylene dithiocyanate (6317-18-6), Dazomet (533-74-4)	12
2.4	Alkohols		2-Phenoxyethanol (122-99-6), Ethanol (64-17-5), Propan-2-ol (67-63-0), Propan-1-ol (71-23-8), DCPP (3380-30-1), Chlorcresol (59-50-7), Biphenyl-2-ol (90-43-7), Sodium 2-biphenylate (132-27-4), Clorofene (120-32-1)	24
2.5	Acids		Nonanoic acid (112-05-0), Octanoic acid (124-07-2), Decanoic acid (334-48-5), L-(+)-lactic acid (79-33-4), Glycolic acid (79-14-1), Formic acid (64-18-6), Benzoic acid (65-85-0), Salicyclic acid (69-72-7), Citric acid (77-92-9), Bromoacetic acid (79-08-3)	22
2.6	Inorganic		Calcium dihydroxide (1305-62-0), Calcium oxide (1305-78-8), Calcium magnesium oxide (37247-91-9), Calcium magnesium tetrahydroxide (39445-23-3), Copper (7440-50-8), Copper sulphate pentahydrate (7758-99-8), Sulphur dioxide (7446-09-5), Ammonium sulphate	14

Class	Reactive molecules/moieties	Sub-groups	Represented biocidal active substances	No. of approval processes
			(7783-20-2; 7704-34-9), Ammonium bromide (12124-97-9)	
2.7	Isathiazoles		BIT (2634-33-5), OIT (26530-20-1), MIT (2682-20-4), CMIT (55965-84-9), DCOIT (64359-81-5), TCMTB (21564-17-0)	10
2.8	QACs		ADBAC (C12-18) (68391-01-5),Quaternary ammonium compounds, C12-14-alkyl[(ethylphenyl)methyl]dimethyl chlorides (85409-23-0), Quaternary ammonium compounds, benzyl-C12-14-alkyldimethyl chlorides (85409-22-9), Amines-C10-16-alkyldimethyl, N-oxides (70592-80-2), Quaternary ammonium compounds, di-C8-10-alkyldimethyl chlorides (68424-95-3), DDAC (7173-51-5), Ampholyt 20 (139734-65-9), Bardap 26 (94667-33-1), CTAC (4080-31-3), DTSACl (27668-52-6), MES (3006-10-8), Quarternary ammonium compounds, benzyl-C12-18-alkyldimethyl, salts with 1,2-benzisothiazol-3(2H)-one 1,1-dioxide (1:1) (68989-01-5)	41
2.9	Silver		Silver (7440-22-4), Silver zeolite (130328-18-6), Silver copper zeolite (130328-19-7), Silver chloride (7783-90-6), Silver sodium zirconium hydrogen phosphate (265647-11-8), Silver nitrate (7761-88-8), Silver phosphate glass (308069-39-8), Silver zinc zeolite (130328-20-0), Reaction mass of titanium dioxide and silver chloride	22
2.10	MITC		Metam sodium (137-42-8), Methylene dithiocyanate (6317-18-6), Dazomet (533-74-4)	3
2.11	Others		Sodium dimethyldithiocarbamate (128-04-1), Potassium dimethyldithiocarbamate (128-03-0), Pyrithione zinc (13463-41-7), PHMB(1415;4.7) (1802181-67-4) PHMB(1600;1.8) (27083-27-8), N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (2372-82-9), Pyridine-2-thiol 1-oxide (3811-73-2), Cyanamide (420-04-2), Bronopol (52-51-7), THPS (55566-30-8), Dodecylguanidine monohydrochloride (13590-97-1), Glucoprotamin (164907-72-6), Chlorhexidin digluconat (18472-51-0), Free radicals generated in situ from ambient air or water, Monolinuron (1746-81-2), 1-[2-(Allyloxy)-2-(2,4-dichlorophenyl)ethyl]-1H-imidazole (35554-44-0)	41

The conclusion for 69 biocidal active substances in the list (total number was 126) was that the formation of DBPs would be less relevant. In the list, these biocides are marked by "unlikely" (see Annex B, column "DBP formation potential"). Their biocidal activity is not based on chemical reactions but on physicochemical interactions which for example disturb crucial structures, like cellular membranes by QAC based biocidal a.s., or generate unfavourable abiotic conditions like alcohols or acids.

The conclusion for the remaining 57 biocidal active substances was that they could have relevant potential for the formation of DBPs.

3.3 Estimation of the influence of PT on DBP formation

A DBP is usually a reaction product of the biocidal a.s. with the matrix present during the biocidal application. Therefore, the matrix composition and concentration of both the matrix and the a.s. will have an important impact on DBP formation. Within the regarded PTs the matrix can contain quite a wide range of substances or admixtures relevant for DBP formation. Depending on PT, all kinds of organic and inorganic matter are possible matrix components.

Biocidal active substance used for PT1 and also those used for disinfection of swimming pool water (PT2) will be in direct contact with materials on human skin, hair and partially human excrement. This includes complex organic components like proteins, creatinine, fat but also smaller molecules like amino acids, nucleic acids other organic acids or urea. Similar organic material will also be present in PT3 uses for example during disinfections of animal housings. The detailed composition of the matrix will be different, as the amount of substances in the excrements will be higher compared to PT1 and PT2 but regarding the included organic compounds no significant differences are expected. In PT4 uses also similar matrix contents are expected when production facilities of "animal based" food are disinfected. In case of production facilities for "plant based" food, typical plant matrix contents like lignin, fulvic and humic acid or complex carbohydrates (cellulose) will also be present. However, these plant-typical organic matter will also be present for example in most of animal excrements. Regarding uses in PT11 surface, river or marine water may be the water source for cooling or process water systems. Concerning the matrix contents also in this case organic matter of animal (microbial) and plant sources will be included. In summary, with respect to organic matter the matrix within the regarded PTs will generally have comparable constituents in a wide range of concentrations. However, the detailed composition will differ to a large extent between the PTs but also between particular uses within the same PT.

Besides organic matter, inorganic (mineral) substances will be part of the matrix present during biocidal uses as well. They are accompanying the organic matter from microbial, animal and human sources and will be therefore to some extent also present in biocidal uses of all regarded PTs. The inorganic matrix components can react to form a limited number of known DPBs (El-Athman et al., 2021; Michalski and Mathews, 2007, Righi et al., 2014; Teo et al., 2015). Additionally, some of them, e.g. chloride, bromide or iodide, are forming reactive intermediates, such as active chlorine, bromine and iodine, which subsequently react with the present organic matter. These is the most probable explanation, why brominated DBPs are formed after a disinfection with a biocidal product using chlorine as reactive molecule (Parinet et al., 2012, Boudenne et al., 2017) or why chlorinated DBPs are formed after a disinfection with a biocidal product using a peroxide or ozone as reactive molecule (Zhang et al., 2013, Shah et al., 2015). Alternatively, brominated and iodinated DBP can be formed by substitution reactions after an initial formation of chlorinated DBP (Westerhoff et al., 2004)

Compared to the matrix contents, the effects of matrix concentration on the formation of DPB are easier to asses. The matrix is direct reaction partner for the formation of DBPs. As a first estimate it can be assumed that as long as the biocidal active substance is present in excess an increasing amount of matrix will lead to an increasing formation of DBPs. Corresponding experiments are described in the literature (Kanan et al., 2015, Delpla et al., 2021). In practice, this relationship will interfere with other effects occurring during a disinfection process. DBPs initially formed may undergo further reactions with the biocidal active substance to form other DPBs and may influence the reaction rates with the primary matrix. Moreover, the amount of matrix may also influence pH value or the hardness of the aqueous medium being disinfected that are relevant reaction parameters for DBP formation (Hansen et al. 2012, Obolensky et al. 2008, MCCormick at al., 2010).

However, the effects of matrix concentration on DBP formation cannot in general be directly connected with particular PTs. Although strictly regulated, the DBP formation potential of biocidal uses in PT5 will depend on the water used as source for the drinking water. Ground water will be mostly free of organic matter. Consequently, the DBP formation potential is low or even very low compared to surface waters (rivers or reservoir lakes) used as drinking water source containing more organic matter. Similar cases also exist among the other PTs. Coolant systems are sometimes run with supply (drinking) water having a low matrix loading. In contrast matrix loading will be high for coolant systems run with marine water or being used in heavy industries. Similar opposites can be found also in PT2 uses. Swimming pool water will have a high matrix loading at time point of the disinfection process. The surfaces in a hospital will be thoroughly cleaned before disinfection, consequently much lower matrix loading is expected. Summing up, the DBP formation potential cannot be directly correlated with the PTs. It is rather a particular use or even a particular application case with high amounts of matrix present, where DBP formation potential will be potentially high.

The reactivity of organic compounds is often influenced by water. Water serves generally as a solvent but also influences the reactivity of numerous functional groups for example by protonating or deprotonating them. If no or only limited amounts of water are present during a disinfection use also the amount of dissolved inorganic compounds like bromide will be influenced. As presence of bromide or iodide has an impact on DPB formation (Parinet et al., 2012, Boudenne et al., 2017), the presence and amount of water can thus be an important factor for DPB formation leading to different reactions and changing the type of DBP produced. Among the disinfection uses two cases can be differed concerning the amount of water present. The disinfection process will take place in water. This is for example the case in PT5, PT11 and swimming pool water (PT2). On the other side water will be much more limited during the disinfection of hard surfaces in the health sector (PT2) or food industry. The literature gives no particular information on this topic but it is addressed in the experimental part of the present project (see chapter 6).

3.4 Use volumes biocidal active substances

To assess the relevance of DBPs it would be necessary to calculate the overall amount generated in biocidal uses. However, the overall amount of generated DBPs is directly depending on the total use of the respective DBP-forming biocidal a.s.. This data would be necessary to establish a reasonable estimation of total amounts of generated DBPs. This data must include the volumes of biocidal active substances used in each particular PT or even better a particular use, as the amount of DBPs entering the environment will, besides the applied volume, depend on the PT or the particular use. However, this data is not available, neither for the German market nor for the European market. In Germany, the BAuA database of registered biocidal products (BAuA-

Melderegister) is available. This database contains information on all biocidal products that have been registered in Germany. The database can be searched for biocidal product names, registration numbers, biocidal a.s., their CAS- or EC-numbers and the PTs. However, the search results contain no data on the use volumes of the particular products and also no data on the biocidal a.s. concentration in the products, both needed to calculate the total use volume of a particular biocidal a.s. within a given PT. Therefore, only the quite general information on the total number of registered biocidal products within a particular PT is available, but this data can only be regarded as a qualitative estimate for the relevance of a biocidal a.s.. A comprehensive overview on the usage of biocidal active substances was prepared within a study conducted by COWI on behalf of the European Commission (COWI, 2009). The evaluated data originates from the time period 1998 – 2001 therefore conclusions for the present situation must be regarded with care. Nevertheless, some of the results are consistent with the present situation or are at least expected to be fairly similar. According to COWI the estimated annual total volume of sales of biocidal a.s. (production and imports) in the EU was about 400,000 tonnes. The actual amount is expected to be higher, due to the entry of the eastern European countries into the EU in the years 2004 and 2007. The majority of those substances were used as disinfectants. The percentage of the biocidal a.s. used within the PTs according to COWI 2009 is expected still to be comparable with the present situation. The highest amounts of biocidal a.s. are used in PT 2 (50.5%) and PT 5 (12.3%) and the sum used as disinfectants (PTs 1-5) is 74.3%. Amended by the amounts in PT 11 (12.5%) and PT12 (1.6%), which are also considered within the present project, the biocidal active substances regarded in this project cover 88.4% of the total volume of applied biocidal a.s.. Consequently, also a majority of the formed DBPs can be expected within the regarded PTs. However, also the COWI project does not include the detailed volumes of biocidal active substances used within particular PTs.

Detailed data on consumption volumes are available for Denmark (Lassen et al., 2001, data based on approx. year 2000), Switzerland (Bürgi et al., 2007, data based on approx. year 2005, not member of EU) and Belgium (SFP, 2012, data based on approx. year 2011). However, the populations of these countries are small and therefore not necessarily representative for the entire EU.

Other approaches to calculate the total use volumes of particular biocidal active substances could not be identified. Using total production and import volumes is not reasonable, as important biocidal active substances like hypochlorite or hydrogen peroxide are not only used as disinfectants.

The companies using biocidal active substances for disinfection are represented by numerous industrial bodies. Requesting the necessary data from them would be quite extensive, they do not necessarily own the required data and, in case the data is available, industrial bodies are not obliged to share this data. As only a complete or nearly complete data set of the use volumes would be useful for a reasonable further evaluation, requesting industrial bodies was not considered an option in this project.

For these reasons, potential amounts of DBPs being released into the environment were not estimated in this project.

3.5 Preliminary conclusions

Biocidal active substances can be categorised according to their potential to form DBPs based on their chemical structure. However, the types and amounts of DBPs resulting from their use cannot be generally derived based on specific categories such as the PT in which an a.s. is assessed. In summary, with respect to organic matter the matrix within the regarded PTs will

generally have comparable constituents in a wide range of concentrations. However, the detailed composition will differ to a large extent between the PTs but also between particular uses within the same PT. Next to matrix composition and concentration, also the presence and amount of water can be an important factor for DPB formation leading to different reactions and changing the type of DBP produced.

4 Linking biocidal active substances to DBPs

A goal of this project was to link the results of the literature search (chapter 2) and the biocidal a.s. that were identified to form DBPs (annex B). However, as described in chapter 2.3.5, the literature data did often not specify exactly which regulatory defined biocidal a.s. was used to generate the DBPs analysed in the experiments. For this reason, it was not possible within the project to directly link the biocidal a.s. to the DBPs from literature. To be nevertheless able to specify which DBPs might result from the use of a biocidal a.s., the categorisation system was developed to categorize the biocidal a.s. in a system that suited the results from literature (chapter 3.2.2).

This categorisation system of the a.s. is based on the chemical structure and better fits the focus of literature data on the reactive molecules that are driving the reactions and thus the formation of DBPs. Following the categorisation presented in Table 3 and combining an overview of all reactive molecules expected to form DBPs with the results of the literature search and the PTs that are relevant for the respective reactive molecules shows existing data gaps (Table 4).

Table 4: Number of potentially DBP forming biocidal a.s. sorted by reactive molecule

Reactive molecule	Categorisation according to chemical structure	Number of represented a.s.	PT	Identified DBP (at least for one of the a.s. class)
Hypochlorite	1.1	10	1-5, 11, 12	Yes
Hypobromite	1.2	9	2, 4, 11, 12	Yes
Iodine	1.3	2	1,3,4	No
Monochloramine	1.4	4	5, 11, 12	Yes
Chlordioxide	1.5	7	2-5, 11, 12	Yes
Ozone	2.1	1	2, 4, 5 ,11	Yes
Peroxide	2.2	11	1-5, 11, 12	Yes
Aldehydes	2.3	11	1-4, 11, 12	No
Bromoacetic acid	2.5	1	4	No
Cyanamide	2.11	1	3	No
Free radicals	2.11	1	3-5, 11, 12	No
Sulfurdioxid	2.6	1	4	No

Proofs of DBP formation were found for all halogenating biocidal a.s. with exception of iodine. However, considering the numerous biocidal a.s. represented by hypobromite, only a low number of 2 references describe DBPs. Furthermore, DBPs are known in the literature for biocidal a.s. acting by oxidation. In total, for 15 biocidal a.s. identified as potentially DBP forming, no information on DBP formation is found in the literature.

Reaction processes described in literature references, in which several biocides were used simultaneously were classified in different ways. In the first consideration, it was tried to find out whether a certain active substance is formed in the process. An example is the use of strongly oxidizing substances with salts containing chloride and/or bromide. In this case, the oxidative biocide serves exclusively to generate hypochlorite or hypobromite from chloride or

bromide and thus, according to the categorisation, falls into halogenated a.s. classes 1.1.3 or 1.2.2. If, on the other hand, it is known from the literature that the disinfection effect is achieved by both biocides, such as upstream ozonation and subsequent chlorination using sodium hypochlorite, reacting separately or side by side, then both a.s. categories were entered in the table, the one for the ozone (2.1) as well as for sodium hypochlorite (1.2.1). A reason for the double entry is justified here, since depending on the matrix and application (product type), it is not clearly shown how exactly the corresponding DBP is formed.

DBP formation identified for one biocidal active substance or the reactive molecule of the category defined in Table 3 is assigned to all biocidal a.s. in the respective category.

For a more detailed overview of the DBPs that could potentially be formed by biocidal a.s., a separate Excel document was developed (download via https://www.umweltbundesamt.de/publikationen, name of the document: "FKZ 3718 65 403 0_Excel annex to DBP project"), containing the following:

- Detailed data from the literature search on DBPs (spreadsheets "DBP_Halogenated DBPs" and "DBP_Non-halogenated DBPs", see chapter 2.3)
- Table linking all DBPs identified in the literature search to the reactive molecules that are known to form them (see Figure 2)

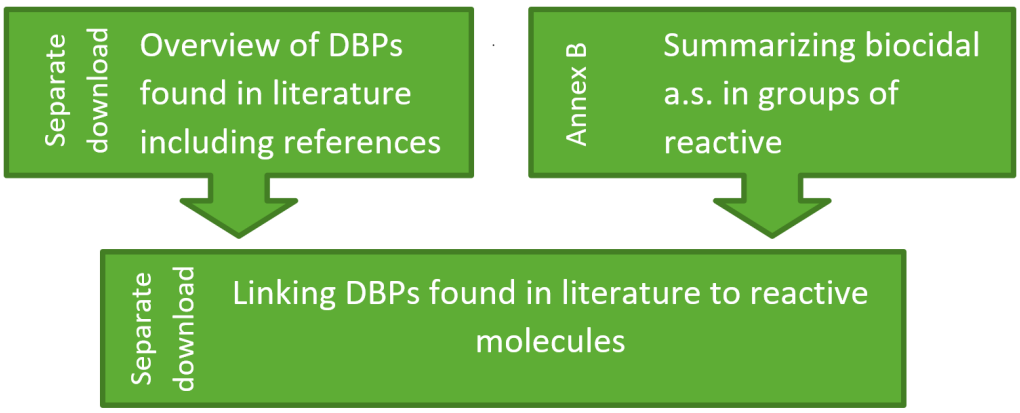
Figure 2: Structure of Excel-Table linking DBPs to reactive molecules

DBP	CAS-Nummer	Active substance in literature leading to DBP-formation	Categories of biocidal active substances leading to DBP-formation																														Substance class of DBP
			1.0	1.1	1.1.1	1.1.2	1.1.3	1.2	1.2.1	1.2.2	1.3	1.4	1.5	2.0	2.1	2.2	2.3	2.3.1	2.3.2	2.4	2.5	2.6	2.7	2.8	2.9	2.10	2.11							
			Halogenated a.s.	Hypochlorite	Organic	Inorganic	In-situ	Hypobromite	Organic	In-situ	Iodine	Monochloramine	Chlordioxid	Non-halogenated a.s.	Ozone	Peroxides	Aldehydes	Organic	In-situ	Alkohols/Phenols	Acids	Inorganic substances	Isathiazoles	QACs	Silver	Methyl isothiocyanate (MITc)	Others							
2,2-dichloroacetamide	683-72-7	combination of ozone, UV and chlorination or chloramination, chlorine, monochloramine, ozone, hypochlorite, chlorination, chloramination, UV + hypochlorite/chloramine		x	x	x	x		x			x	x		x																		Haloacetamides

Source: own illustration, structure of Excel table linking DBPs to reactive molecules.

The specific biocidal a.s. being summarised under the respective reactive molecules can be looked up in Annex B.

Figure 3: Structure of results presentation



Source: own illustration, structure of results presentation

5 Analysis of the entry routes into the environment

5.1 Introduction

Based on the results of the two previous chapters, the potential entry routes of DBPs into the relevant environmental compartments were analysed and compared to the entry routes of the active substances. The key process for this evaluation were the initial release into the environment (water, air, slurry, soil).

As part of this analysis, it is suggested to consider the half-life of the active substances as trigger to decide whether partitioning between environmental compartments is to be expected. If the necessary experimental data is not available for the DBP it is assumed that different distribution from a.s. and DBPs is likely.

As DBPs are quickly formed before they reach the environment, it was important to analyse the distribution of the biocidal active substance and DBP already during the use. A respective screening calculation was suggested that was based on the partition coefficients between water and air (Kaw). In order to evaluate also the fate in a wastewater treatment plant, the partition coefficient between water and soil (Koc) was used in a second step. As this calculation would be based on equilibrium conditions without degradation, this step was best comparable with the principles of a Mackay I simulation. However, the number of compartments in this step was reduced compared to a full model simulation. Input parameters needed at this level were limited to distribution data. So, simply the results of EPI-Suite estimations could be used to obtain the input parameters for these calculations. However, it has to be kept in mind that using input parameter from EPI-Suite estimations and Mackay I as a trigger for different distribution (mode of entry) are subjected to some restrictions (uncertainties).

For the input parameter, information from the publicly available assessment reports/competent authority reports (AR/CAR) was used in this study if one of the active substances was already approved. If this was not the case, it has to be beard in mind that the values might change after evaluation during the approval process.

5.2 Procedure

Generally, if the DBP is a substance of concern for the environmental risk assessment depends on

- the quantity which is released into the environment,
- the entry route into the environment (via air and/or waste water and/or sludge/slurry), and
- the ecotoxicity of the DBP.

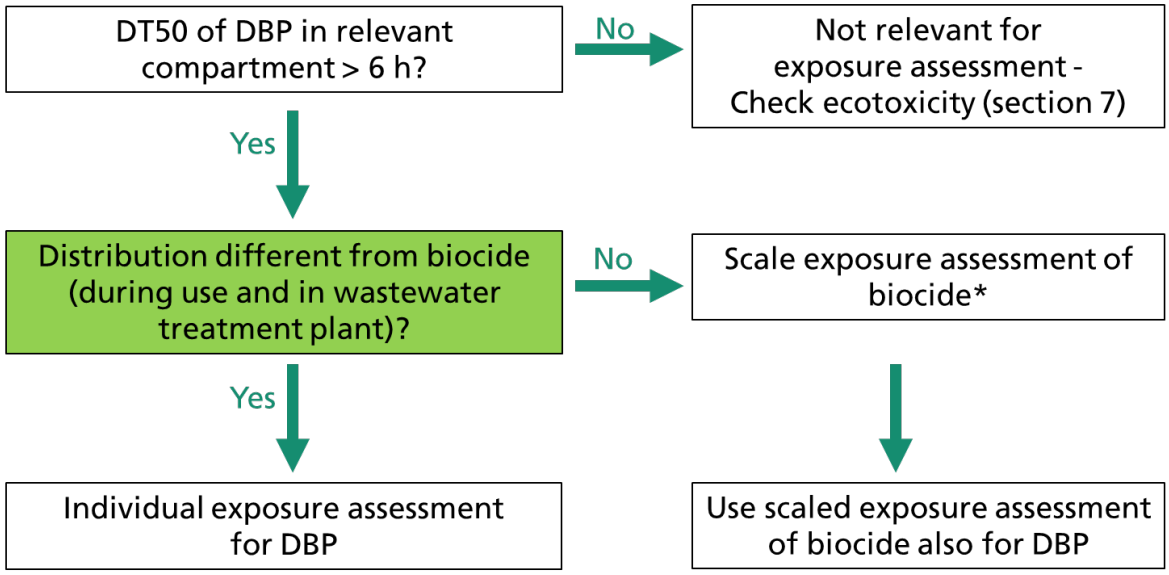
In order to address these points, following parameters had to be considered:

- The quantity, which is released into environment, depends on the formation fraction of the DBP, i.e. how many molecules are formed relative to the total number of active substance molecules. However, even if the DBP is significantly formed it does not necessarily mean that significant amounts will reach the environment as long as it is relatively instable.
- With regard to the entry route into the environment, it is essential to check whether the DBP distributes differently or similarly. It is assumed that a DBP will only be of relevance for the environmental risk assessment if it partitions differently into the environmental

compartments. If so, the risk assessment already performed for the a.s. may not cover the DBP and an additional risk assessment for the transformation product (= DBP) has to be performed.

- Finally, also the ecotoxicity of the DBP (compared to the ecotoxicity of the a.s.) is an important aspect for the relevance of DBPs. However, this is not an exposure related point and was not part of the project.

Figure 4: Flowchart describing the relevance of an individual exposure assessment for DBPs



* based on formation fraction and on molar ratio but without biocide degradation

Source: own illustration, relevance of an individual exposure assessment for DBPs

Whether a DBP is relevant depends on the time of application, i.e. if the DBP has enough time to react until it will be released to the sewer or the environment. However, the life-time of these DBPs depends very often on the matrix as well. In addition, if the DBPs will be released to the sewer, there is some time until it reaches the STP, and within the STP, the molecules have time to react until the substance will be released into the environment.

Moreover, in the risk assessment emission will usually be standardized on a one day basis. For the sewer this will be diluted with the amount of wastewater of one day, and diluted after the STP within the river flow of one day. A half-life of < 6 h corresponds to a degradation of > 90% in one day. Finally, it has to be discussed which half-life is relevant for the decision on relevance of DBP. Often disinfection is in aqueous solution. For this reason, the relevant compartment for the life-time is probably the water compartment. If the DBP are released down the drain, maybe the half-life in the STP is relevant or the life-time until reaching the STP. For direct release probably the half-life in surface water is more suitable.

An overview about the procedure is presented in Figure 4. In the first step, it was checked whether the DT50 of the DBP in the relevant compartment (i.e., water in most situations) was longer than 6 h. If the DT50 was shorter than 6 h it was assumed that there will be no time to reach any environmental compartment. 6 h are also the hydraulic retention time in the sewage treatment plant in EUSES (TSA 2008). This is supported by various studies. As regards, sewer transit time, a robust study by Ort et al., 2014 reported sewer transit times (obtained by survey data for facilities) for 31 wastewater treatment facilities across Europe. The average sewer

transit time was 4.6 h, minimum was 1 h, and maximum was 12 h. In addition, sewer residence times from monitoring studies for specific wastewater facilities have been reported for parts of Europe, including the UK (mean 2 h) and Rome (3–5 h) (Johnson and Williams, 2004). Kapo et al. (2017) recently completed a robust assessment of sewer transit times in the US and found that the mean travel time was 3.3 h. These data further support the data provided in the Ort et al. (2014) study.

The trigger of 6h, however, is not applicable for applications with direct emissions to the environment via manure, surface water or soil, for example. For this reason, the flowchart is not applicable for product types 3 or 11 or applications via fumigation or vaporization.

In case the half-life of the DBP is above 6 h, the distribution of the DBP and the active substance during the use should be compared with regard to significant different behaviour. Two scenarios were suggested:

- use with small water volumes (e.g., surface disinfection) or
- use with large water volumes (e.g., swimming pool).

For both scenarios, equilibrium conditions were assumed for the calculation. Furthermore, it is assumed that the area of the water is the same as the air compartment (e.g., disinfection of a floor). The following equation (1) shows the calculation of the air fraction:

$$f_{air}\,(\%) = K_{aw} \cdot \frac{h_{air}}{h_{Water}} \cdot 100 \qquad (1)$$

f_{air}: substance fraction in air (%)

Kaw: air – water distribution coefficient (-)

h_{air}: height of the air compartment (-)

h_{water}: height of the water compartment (-)

As it is possible that active substance and DBP behave similarly (with regard to the distribution) during the use but differently later in a simple treatment plant, a second check is proposed considering the substance fraction in sludge using equation (2):

$$f_{sludge} = \frac{Koc \cdot f_{solid} \cdot \frac{OC}{100}}{Koc \cdot f_{solid} \cdot \frac{OC}{100} + 1} \cdot 100 \qquad (2)$$

f_{sludge}: substance fraction in sludge (%)

Koc: Partition coefficient organic carbon / water (L/kg)

f_{solid}: fraction of solid particles in the water of the treatment plant (-)

OC: organic carbon content of the sludge (30%)

If no different behaviour is expected for active substance and DBP then the scaled exposure assessment of the active substance can be used also for the DBP. Scaling should be based on the formation fraction of the DBP during use (i.e., how many DBP molecules are formed by a given number of active substance molecules, expressed as ratio) and the ratio of the molar masses of active substance and DBP (see equation (3)). If the formation fraction of the DBP is not available, a value of 1 should be set instead. It has to be kept in mind, that the formation fraction depends

on several external parameters influencing each other and the formation fraction itself (see chapters 2.3 and 6). Based on this, it remains unclear how to determine the worst-case formation fraction in experiments. Always using a formation fraction of 1, on the other hand, will lead to overestimation of risks. This then require refinement, leading again to the unsolved question of worst-case experiments. Active substance degradation should not be considered since it is possible that its half-life is shorter than the half-life of the DBP.

$$PEC_{DBP} = PEC_{biocide} \frac{f_{DBP} \cdot M_{DBP}}{M_{biocide}} . \qquad (3)$$

f_{DBP}: formation fraction of the DBP

$PEC_{biocide}$: PEC calculated for the biocide (without degradation)

PEC_{DBP}: PEC calculated for the DBP

M_{DBP}: Molar mass of the DBP (g/mol)

$M_{biocide}$: Molar mass of the biocide (g/mol)

Only if the distribution of the DBP during use or later in the wastewater treatment plant was significantly different from the active substance behaviour, an individual exposure assessment for the DBP would be necessary. The initial release should be again based on the formation fraction and the molar ratio of the molar masses.

Suggestions for the scenario parameters needed for the calculation are presented in Table 5.

Table 5: Properties of the swimming pool and the surface disinfection scenario

Scenario parameter	Swimming pool	Surface disinfection
f_{air}	10	6
h_{water}	2.5	0.0001
f_{solid}	0.1	0.1
OC°	30	30

° taken from the sewage treatment plant in EUSES, primary settler (TSA 2008)

Finally, a trigger must be defined that decides whether biocidal a.s. and DPB show a different distribution. For example, if the active substance is solely emitted to the sewer, and the DBP is probably mainly emitted to air, it is not acceptable that the risk assessment of the active substance is adequate for the DBP, even if a safety factor is used.

This will be complicated for the evaluation of the trigger with regard to the distribution in the STP, and in the environment such as distribution to sediment after the STP. In this case lower percentage concentration of the DBP in water is covered by the water risk assessment of the active substance, but the higher concentration in sludge or sediment probably not. For example, if the active substance is emitted to 100% to water, and not adsorbed to sludge or sediment a difference of 10% or higher in the water is acceptable for the DBP to be covered by the risk assessment of the active substance for the water compartment, but using active substances sediment risk assessment (or soil risk assessment) is probably not acceptable if the adsorption increases for the DBP.

Overall, a trigger of 10% to differentiate between different or similar behaviour of a.s. and DBP seems to be plausible. However, there is currently no reference available for this trigger. It has to be discussed in the future which value may be adequate. For this screening approach within this project, it is proposed to consider 10% difference for the distribution of biocide and DBP in one of the compartments as criteria for "different behaviour".

5.3 Illustrative example

In this chapter, a typical active substance was analysed with regard to the entry routes of formed DBPs into the relevant environmental compartments: hypochloric acid (hypochlorite). Hypochlorite represents the active molecule in the chlorine based a.s. There was no information available in the AR/CAR whether any of the DBP fulfils the requirement of 6 h for the DT50 in water. Therefore, it was assumed based on EPIsuite that all DBPs have a half-life > 6 h and the distribution check was performed for 67 potential DBPs. The chosen DBPs were selected from the DBPs found in the literature search (chapter 2). The selection intended to consider as much of the different structures and thus physico-chemical properties of the identified DBPs as possible. The considered DBP were identified in connection to the particular a.s. based on the literature search (see chapter 2).

The distribution parameters considered for hypochlorite and the DBPs are shown in Table 6. Unfortunately, for many of the DBP no measured input data was available. In order to have a consistent data set, the assessment tool EPI suite was used to obtain the input data for Kaw and Koc. The distribution coefficient for hypochlorite (log Kaw of -4,35) was taken from the respective assessment report. As no experimental Koc value was available in the assessment report, also this Koc value was calculated by EPI suite to 0.001075 L/kg.

In the annex C (Table 28 - Table 35), additional examples are presented for other a.s. The DBP considered for a particular a.s. were chosen from a selection of 80 potential DBPs but for each a.s. the choice was reduced to the DPB were identified in connection to the particular a.s.. When using EPI suite, it has to be considered that it cannot be used to calculate the Kaw for inorganic compounds. Therefore, for the following active substances the Kaw was either obtained from the AR or based on the compilation of Henry's Law constants by Rolf Sander (1999). The Henry's law constant was transformed into the Kaw considering a temperature of 25 °C.

- ClO_2: -1.389, Lide and Frederikse (1995)
- H_2O_2 -6.308 Assessment report (1995)
- HOBr -5.174 Frenzel et al (1998)
- O_3 0.570 Jacob (1986)
- HOCl -4.353 Assessment report (1995)

In the Table 6, the input parameters for the DBP and the a.s. considered in the analyses are presented.

Table 6: Input data used for the calculation of the distribution

CAS	Substance	Log Kaw (-)	Kaw (-)	Koc (L/kg)
10049-04-4	**Chlordioxid**	**-1.39**	**0.041**	**0.00**
007722-84-1	**Hydrogen peroxide**	**-6.52**	**3E-07**	**1.60**

CAS	Substance	Log Kaw (-)	Kaw (-)	Koc (L/kg)
13824-96-9	**Hypobromite**	**-5.17**	**7E-06**	**0.00**
10028-15-6	**Ozone**	**0.57**	**3.715**	**0.18**
7681-52-9	**Hypochlorite**	**-4.35**	**4E-05**	**0.00**
000084-65-1	9,10-Anthracenedione	-10	1E-10	5011.87
000506-68-3	Cyanogen bromide	-10	1E-10	14.35
001318-59-8	Chlorite	-10	1E-10	0.00
000099-06-9	Benzoic acid, 3-hydroxy-	-9.335	5E-10	14.20
019643-45-9	2,6-dibromo-1,4-benzoquinone	-8.704	2E-09	248.10
000598-70-9	Acetamide, 2,2-dibromo-	-8.215	6E-09	9.36
077439-76-0	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furan	-7.998	1E-08	11.83
000099-28-5	Phenol, 2,6-dibromo-4-nitro-	-7.843	1E-08	0.00
000062-23-7	Benzoic acid, 4-nitro-	-7.757	2E-08	26.32
000634-85-5	2,3,5-Trichloro-1,4-benzoquinone	-7.731	2E-08	597.40
000697-91-6	2,5-Cyclohexadiene-1,4-dione, 2,6-dichloro-	-7.588	3E-08	320.10
005278-95-5	Dibromochloroacetic acid	-6.98	1E-07	11.27
003964-57-6	3-Chloro-4-hydroxybenzoic acid, Methyl ester	-6.96	1E-07	0.00
000075-87-6	Acetaldehyde, trichloro-	-6.925	1E-07	17.52
000107-22-2	Ethanedial	-6.866	1E-07	0.35
000075-96-7	Acetic acid, tribromo-	-6.865	1E-07	12.64
000069-72-7	Benzoic acid, 2-hydroxy-	-6.523	3E-07	37.38
071133-14-7	Bromodichloroacetic acid	-6.495	3E-07	10.05
000079-43-6	Acetic acid, dichloro-	-6.465	3E-07	4.62
000079-11-8	Acetic acid, chloro-	-6.422	4E-07	1.89
000076-03-9	Acetic acid, trichloro-	-6.258	6E-07	2.00
000059-89-2	N-Nitrosomorpholine	-5.999	1E-06	3.53
000118-79-6	Phenol, 2,4,6-tribromo-	-5.838	1E-06	0.00
000930-55-2	Pyrrolidine, 1-nitroso-	-5.699	2E-06	5.98
000075-99-0	Propanoic acid, 2,2-dichloro-	-5.636	2E-06	2.51
006837-24-7	2-Pyrrolidinone, 1-cyclohexyl-	-5.63	2E-06	54.54

CAS	Substance	Log Kaw (-)	Kaw (-)	Koc (L/kg)
000464-10-8	Methane, tribromonitro-	-5.579	3E-06	0.00
000115-17-3	Acetaldehyde, tribromo-	-5.371	4E-06	31.87
000106-41-2	Phenol, 4-bromo-	-5.209	6E-06	0.00
000050-00-0	Formaldehyde	-4.861	1E-05	7.75
003252-43-5	Acetonitrile, dibromo-	-4.78	2E-05	37.78
000598-91-4	Methane, dibromonitro-	-4.641	2E-05	0.00
000632-21-3	2-Propane, 1,1,3,3-tetrachloro-	-4.506	3E-05	29.46
000100-75-4	Piperidine, 1-nitroso-	-4.462	3E-05	12.04
003039-13-2	Acetaldehyde, dibromo-	-4.434	4E-05	8.81
000086-30-6	Benzenamine, N-nitroso-N-phenyl-	-4.306	5E-05	410.40
002648-61-5	Ethanone, 2,2-dichloro-1-phenyl-	-4.302	5E-05	194.00
083463-62-1	Bromochloracetonitrile	-4.295	5E-05	33.69
000545-06-2	Acetonitrile, trichloro-	-4.261	5E-05	297.40
000119-61-9	Methanone, diphenyl-	-4.101	8E-05	426.58
000624-75-9	Iodoacetonitrile	-4.031	9E-05	45.15
010595-95-6	N-Nitrosomethylethylamine	-3.952	0.0001	8.01
023676-09-7	Ethyl 4-ethoxybenzoate	-3.83	0.0001	806.70
000055-18-5	Ethanamine, N-ethyl-N-nitroso-	-3.829	0.0001	14.03
003018-12-0	Dichloroacetonitrile	-3.81	0.0002	30.04
000563-70-2	Bromonitromethane	-3.703	0.0002	0.00
007119-89-3	Methane, dichloronitro	-3.67	0.0002	0.00
000621-64-7	1-Propanamine, N-nitroso-N-propyl-	-3.658	0.0002	43.03
000079-02-7	Acetaldehyde, dichloro-	-3.463	0.0003	7.00
000143-07-7	Dodecanoic acid	-3.42	0.0004	501.30
000098-86-2	Ethanone, 1-phenyl-	-3.371	0.0004	63.10
000107-14-2	Acetonitrile, chloro-	-3.355	0.0004	36.83
000924-16-3	1-Butanamine, N-butyl-N-nitroso-	-3.268	0.0005	216.90
001794-84-9	Methane, chloronitro-	-3.218	0.0006	0.00
000623-48-3	Acetic acid, iodo-, ethyl ester	-3.148	0.0007	0.00
000107-20-0	Acetaldehyde, chloro-	-3.01	0.001	5.57
000100-52-7	Benzaldehyde	-2.962	0.0011	32.69

CAS	Substance	Log Kaw (-)	Kaw (-)	Koc (L/kg)
000075-47-8	Methane, triiodo-	-2.903	0.0013	425.90
010599-90-3	Chloramide	-2.567	0.0027	0.09
000075-07-0	Acetaldehyde	-2.564	0.0027	3.22
000593-94-2	Dibromoiodomethane	-2.525	0.003	81.09
000123-38-6	Propanal	-2.523	0.003	10.52
000132-64-9	Dibenzofuran	-2.06	0.0087	8128.31
034970-00-8	Bromochloroiodomethane	-2.04	0.0091	67.74
018829-56-6	2-Nonenal, (E)-	-2.025	0.0094	244.60
000090-12-0	Naphthalene, methyl-	-1.677	0.021	2290.87
000075-25-2	Methane, tribromo-	-1.66	0.0219	114.82
000594-04-7	Dichloroiodomethane	-1.555	0.0279	57.73
000124-48-1	Methane, dibromochloro-	-1.495	0.032	83.18
000593-71-5	Chloroiodomethane	-1.448	0.0356	39.49
000112-31-2	Decanal	-1.133	0.0736	596.50
000076-06-2	Methane, trichloronitro-	-1.077	0.0838	0.00
000075-27-4	Methane, bromodichloro-	-1.062	0.0867	60.26
000683-72-7	2,2-dichloroacetamide	-0.901	0.1256	84.77
000067-66-3	Methane, trichloro-	-0.824	0.15	39.81

Input data for active substances in bold characters
Koc values reported with two decimals

The results of the calculation for the scenario “large water volume” (swimming pool) during use are shown in Table 7. In total, 10% and 73% of the DBP in Table 7 showed different distribution in water or air and sludge, respectively. Obviously, most of the DBP behaved similarly during the use but later showed different behaviour in the waste water treatment plant. Single substance assessment would be needed for 49 (75%) DBPs, based on our concept.

Table 7: Distribution for hypochlorite and corresponding DBP for the scenario “lage water volume during use”

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
7681-52-9	**Hypochlorite**	**99.98**	**0.00**	-	-	-
000084-65-1	9,10-Anthracenedione	100.00	99.34	No	Yes	different
000506-68-3	Cyanogen bromide	100.00	30.09	No	Yes	different
001318-59-8	Chlorite	100.00	0.00	No	No	comparable

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
019643-45-9	2,6-dibromo-1,4-benzoquinone	100.00	88.16	No	Yes	different
000598-70-9	Acetamide, 2,2-dibromo-	100.00	21.92	No	Yes	different
077439-76-0	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furan	100.00	26.19	No	Yes	different
000099-28-5	Phenol, 2,6-dibromo-4-nitro-	100.00	0.00	No	No	comparable
000634-85-5	2,3,5-Trichloro-1,4-benzoquinone	100.00	94.72	No	Yes	different
000697-91-6	2,5-Cyclohexadiene-1,4-dione, 2,6-dichloro-	100.00	90.57	No	Yes	different
005278-95-5	Dibromochloroacetic acid	100.00	25.27	No	Yes	different
003964-57-6	3-Chloro-4-hydroxybenzoic acid, Methyl ester	100.00	0.00	No	No	comparable
000075-87-6	Acetaldehyde, trichloro-	100.00	34.45	No	Yes	different
000107-22-2	Ethanedial	100.00	1.05	No	No	comparable
000075-96-7	Acetic acid, tribromo-	100.00	27.49	No	Yes	different
071133-14-7	Bromodichloroacetic acid	100.00	23.17	No	Yes	different
000079-43-6	Acetic acid, dichloro-	100.00	12.17	No	Yes	different
000079-11-8	Acetic acid, chloro-	100.00	5.38	No	No	comparable
000076-03-9	Acetic acid, trichloro-	100.00	5.65	No	No	comparable
000059-89-2	N-Nitrosomorpholine	100.00	9.57	No	No	comparable
000118-79-6	Phenol, 2,4,6-tribromo-	100.00	0.00	No	No	comparable
000930-55-2	Pyrrolidine, 1-nitroso-	100.00	15.20	No	Yes	different
000075-99-0	Propanoic acid, 2,2-dichloro-	100.00	7.01	No	No	comparable
006837-24-7	2-Pyrrolidinone, 1-cyclohexyl-	100.00	62.07	No	Yes	different
000464-10-8	Methane, tribromonitro-	100.00	0.00	No	No	comparable
000115-17-3	Acetaldehyde, tribromo-	100.00	48.88	No	Yes	different
003252-43-5	Acetonitrile, dibromo-	99.99	53.13	No	Yes	different
000598-91-4	Methane, dibromonitro-	99.99	0.00	No	No	comparable
000632-21-3	2-Propane, 1,1,3,3-tetrachloro-	99.99	46.92	No	Yes	different
000100-75-4	Piperidine, 1-nitroso-	99.99	26.54	No	Yes	different
003039-13-2	Acetaldehyde, dibromo-	99.99	20.90	No	Yes	different

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000086-30-6	Benzenamine, N-nitroso-N-phenyl-	99.98	92.49	No	Yes	different
002648-61-5	Ethanone, 2,2-dichloro-1-phenyl-	99.98	85.34	No	Yes	different
083463-62-1	Bromochloracetonitrile	99.98	50.27	No	Yes	different
000545-06-2	Acetonitrile, trichloro-	99.98	89.92	No	Yes	different
000119-61-9	Methanone, diphenyl-	99.97	92.75	No	Yes	different
000624-75-9	Iodoacetonitrile	99.96	57.53	No	Yes	different
010595-95-6	N-Nitrosomethylethylamine	99.96	19.37	No	Yes	different
023676-09-7	Ethyl 4-ethoxybenzoate	99.94	96.03	No	Yes	different
000055-18-5	Ethanamine, N-ethyl-N-nitroso-	99.94	29.62	No	Yes	different
003018-12-0	Dichloroacetonitrile	99.94	47.40	No	Yes	different
000563-70-2	Bromonitromethane	99.92	0.00	No	No	comparable
007119-89-3	Methane, dichloronitro	99.91	0.00	No	No	comparable
000621-64-7	1-Propanamine, N-nitroso-N-propyl-	99.91	56.35	No	Yes	different
000079-02-7	Acetaldehyde, dichloro-	99.86	17.36	No	Yes	different
000143-07-7	Dodecanoic acid	99.85	93.77	No	Yes	different
000107-14-2	Acetonitrile, chloro-	99.82	52.49	No	Yes	different
000924-16-3	1-Butanamine, N-butyl-N-nitroso-	99.78	86.68	No	Yes	different
001794-84-9	Methane, chloronitro-	99.76	0.00	No	No	comparable
000623-48-3	Acetic acid, iodo-, ethyl ester	99.72	0.00	No	No	comparable
000107-20-0	Acetaldehyde, chloro-	99.61	14.31	No	Yes	different
000100-52-7	Benzaldehyde	99.57	49.51	No	Yes	different
000075-47-8	Methane, triiodo-	99.50	92.74	No	Yes	different
010599-90-3	Chloramide	98.93	0.28	No	No	comparable
000075-07-0	Acetaldehyde	98.92	8.81	No	No	comparable
000593-94-2	Dibromoiodomethane	98.82	70.87	No	Yes	different
000132-64-9	Dibenzofuran	96.63	99.59	No	Yes	different
034970-00-8	Bromochloroiodo-methane	96.48	67.02	No	Yes	different
018829-56-6	2-Nonenal, (E)-	96.36	88.01	No	Yes	different

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000090-12-0	Naphthalene, methyl-	92.24	98.57	No	Yes	different
000075-25-2	Methane, tribromo-	91.95	77.50	No	Yes	different
000594-04-7	Dichloroiodomethane	89.97	63.40	Yes	Yes	different
000124-48-1	Methane, dibromochloro-	88.66	71.39	Yes	Yes	different
000593-71-5	Chloroiodomethane	87.52	54.23	Yes	Yes	different
000076-06-2	Methane, trichloronitro-	74.91	0.00	Yes	No	different
000075-27-4	Methane, bromodichloro-	74.25	64.38	Yes	Yes	different
000683-72-7	2,2-dichloroacetamide	66.56	71.78	Yes	Yes	different
000067-66-3	Methane, trichloro-	62.50	54.43	Yes	Yes	different

The results of the calculation for the scenario "small water volume" (surface disinfection) during use is shown in Table 8. In total, 88% and 73% of the DBP in the table showed different distribution in water or air and sludge, respectively. Obviously, when considering this scenario most of the DBP behaved differently already during the use but also later in the waste water treatment plant. Single substance assessment would be needed for 66 (100%) DBP, based on our concept.

Table 8: Distribution for hypochlorite and corresponding DBP for the scenario "small water volume during use"

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
7681-52-9	**Hypochlorite**	**27.29**	**0.00**	-	-	-
000084-65-1	9,10-Anthracenedione	100.00	99.34	Yes	Yes	different
000506-68-3	Cyanogen bromide	100.00	30.09	Yes	Yes	different
001318-59-8	Chlorite	100.00	0.00	Yes	No	different
019643-45-9	2,6-dibromo-1,4-benzoquinone	99.99	88.16	Yes	Yes	different
000598-70-9	Acetamide, 2,2-dibromo-	99.96	21.92	Yes	Yes	different
077439-76-0	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furan	99.94	26.19	Yes	Yes	different
000099-28-5	Phenol, 2,6-dibromo-4-nitro-	99.91	0.00	Yes	No	different
000634-85-5	2,3,5-Trichloro-1,4-benzoquinone	99.89	94.72	Yes	Yes	different
000697-91-6	2,5-Cyclohexadiene-1,4-dione, 2,6-dichloro-	99.85	90.57	Yes	Yes	different
005278-95-5	Dibromochloroacetic acid	99.38	25.27	Yes	Yes	different

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
003964-57-6	3-Chloro-4-hydroxybenzoic acid, Methyl ester	99.35	0.00	Yes	No	different
000075-87-6	Acetaldehyde, trichloro-	99.29	34.45	Yes	Yes	different
000107-22-2	Ethanedial	99.19	1.05	Yes	No	different
000075-96-7	Acetic acid, tribromo-	99.19	27.49	Yes	Yes	different
071133-14-7	Bromodichloroacetic acid	98.12	23.17	Yes	Yes	different
000079-43-6	Acetic acid, dichloro-	97.98	12.17	Yes	Yes	different
000079-11-8	Acetic acid, chloro-	97.78	5.38	Yes	No	different
000076-03-9	Acetic acid, trichloro-	96.79	5.65	Yes	No	different
000059-89-2	N-Nitrosomorpholine	94.33	9.57	Yes	No	different
000118-79-6	Phenol, 2,4,6-tribromo-	91.99	0.00	Yes	No	different
000930-55-2	Pyrrolidine, 1-nitroso-	89.29	15.20	Yes	Yes	different
000075-99-0	Propanoic acid, 2,2-dichloro-	87.82	7.01	Yes	No	different
006837-24-7	2-Pyrrolidinone, 1-cyclohexyl-	87.67	62.07	Yes	Yes	different
000464-10-8	Methane, tribromonitro-	86.34	0.00	Yes	No	different
000115-17-3	Acetaldehyde, tribromo-	79.66	48.88	Yes	Yes	different
003252-43-5	Acetonitrile, dibromo-	50.11	53.13	Yes	Yes	different
000598-91-4	Methane, dibromonitro-	42.17	0.00	Yes	No	different
000632-21-3	2-Propane, 1,1,3,3-tetrachloro-	34.83	46.92	No	Yes	different
000100-75-4	Piperidine, 1-nitroso-	32.56	26.54	No	Yes	different
003039-13-2	Acetaldehyde, dibromo-	31.16	20.90	No	Yes	different
000086-30-6	Benzenamine, N-nitroso-N-phenyl-	25.22	92.49	No	Yes	different
002648-61-5	Ethanone, 2,2-dichloro-1-phenyl-	25.04	85.34	No	Yes	different
083463-62-1	Bromochloracetonitrile	24.74	50.27	No	Yes	different
000545-06-2	Acetonitrile, trichloro-	23.31	89.92	No	Yes	different
000119-61-9	Methanone, diphenyl-	17.38	92.75	No	Yes	different
000624-75-9	Iodoacetonitrile	15.18	57.53	Yes	Yes	different
010595-95-6	N-Nitrosomethylethylamine	12.99	19.37	Yes	Yes	different
023676-09-7	Ethyl 4-ethoxybenzoate	10.13	96.03	Yes	Yes	different
000055-18-5	Ethanamine, N-ethyl-N-nitroso-	10.11	29.62	Yes	Yes	different
003018-12-0	Dichloroacetonitrile	9.72	47.40	Yes	Yes	different

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000563-70-2	Bromonitromethane	7.76	0.00	Yes	No	different
007119-89-3	Methane, dichloronitro	7.23	0.00	Yes	No	different
000621-64-7	1-Propanamine, N-nitroso-N-propyl-	7.05	56.35	Yes	Yes	different
000079-02-7	Acetaldehyde, dichloro-	4.62	17.36	Yes	Yes	different
000143-07-7	Dodecanoic acid	4.20	93.77	Yes	Yes	different
000107-14-2	Acetonitrile, chloro-	3.64	52.49	Yes	Yes	different
000924-16-3	1-Butanamine, N-butyl-N-nitroso-	3.00	86.68	Yes	Yes	different
001794-84-9	Methane, chloronitro-	2.68	0.00	Yes	No	different
000623-48-3	Acetic acid, iodo-, ethyl ester	2.29	0.00	Yes	No	different
000107-20-0	Acetaldehyde, chloro-	1.68	14.31	Yes	Yes	different
000100-52-7	Benzaldehyde	1.50	49.51	Yes	Yes	different
000075-47-8	Methane, triiodo-	1.32	92.74	Yes	Yes	different
010599-90-3	Chloramide	0.61	0.28	Yes	No	different
000075-07-0	Acetaldehyde	0.61	8.81	Yes	No	different
000593-94-2	Dibromoiodomethane	0.56	70.87	Yes	Yes	different
000132-64-9	Dibenzofuran	0.19	99.59	Yes	Yes	different
034970-00-8	Bromochloroiodomethane	0.18	67.02	Yes	Yes	different
018829-56-6	2-Nonenal, (E)-	0.18	88.01	Yes	Yes	different
000090-12-0	Naphthalene, methyl-	0.08	98.57	Yes	Yes	different
000075-25-2	Methane, tribromo-	0.08	77.50	Yes	Yes	different
000594-04-7	Dichloroiodomethane	0.06	63.40	Yes	Yes	different
000124-48-1	Methane, dibromochloro-	0.05	71.39	Yes	Yes	different
000593-71-5	Chloroiodomethane	0.05	54.23	Yes	Yes	different
000076-06-2	Methane, trichloronitro-	0.02	0.00	Yes	No	different
000075-27-4	Methane, bromodichloro-	0.02	64.38	Yes	Yes	different
000683-72-7	2,2-dichloroacetamide	0.01	71.78	Yes	Yes	different
000067-66-3	Methane, trichloro-	0.01	54.43	Yes	Yes	different

This example showed that the use of hypochlorite led to a high number of DBPs behaving differently to the active substance and would thus require single substance assessments. In total, single substance assessments would be needed for 66 DBPs for the two tested scenarios. The input parameters of those single substance assessments were often not available and still need to be produced. The main challenge for these single substance assessments is that the formation

fractions of the DBP depend on several parameters and are thus difficult to mimic in the laboratory in a reproducible way.

5.4 Preliminary conclusions

The results of our analyses showed that a large proportion of DBPs behaves differently compared to the active substance. The consequence is that most of the DBPs are not covered by the environmental risk assessment for the active substances and that single substance assessments of the DBPs would need to be conducted to achieve the desired level of protection and follow the precautionary principle.

However, single substance assessments of such a high number of DBPs does not seem realistic and would, despite substantial efforts needed for laboratory experiments, still be associated with several uncertainties due to the complex formation patterns of DBPs. To conclude, the derivation of single substance PECs for DBPs does not seem feasible in the frame of the environmental risk assessments under the BPR.

6 Experimental study of DBPs

6.1 Introduction

In this chapter, the formation of DBPs under different experimental conditions is investigated. The experiments comprise the analysis of samples generated under laboratory conditions as well as samples originating from professional biocide applications.

Originally, the specification of relevant analytical experiments should have resulted from the literature searches described in chapters 2 and 3. By combining the outcome of these two work packages, i.e. biocidal a.s. and corresponding PTs relevant for DBP formation a list of particular relevant DBPs for chemical analysis should have been the result. Finally evaluating possible entry routes into the environment in chapter 5, the biocidal use/DBP combinations most relevant with respect to environmental risk assessment should be chosen for experimental validation.

However, as summarised in chapter 2.3.5, the output of the literature searches is limited with respect to the original intentions. As a consequence, the approach of the experimental part within the present study is modified and following tasks are addressed:

- Choice of a representative list of relevant DBPs for analysis.
- Definition of experimental conditions including the biocidal a.s. covering possible worst-case scenarios of the relevant PTs with respect to DBP formation
- Development of suitable analytical methods for DBP quantification
- Performance of simulated disinfection applications and evaluation considering the detected DBPs and resulting worst-case conditions
- Comparison of DBP formation in the simulated disinfection applications to samples obtained from professional disinfection uses

6.2 Choice of the analysed DBPs, the biocidal a.s. and matrix for laboratory simulations

Choice of the DBPs analysed

The choice of the DBPs considered for the analytical experiments was primarily based on the evaluation of the literature search on DBPs described in chapter 2. The most important criterion was the frequency of occurrence in the evaluated literature to capture the known DBPs. This led to the inclusion of well-known DBP families like trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs) and haloacetaldehydes (HALs). However, another intention of the analytical experiments was the consideration of DBPs covering the broad spectrum of substances found in the literature as far as possible. Consequently, exemplary substances from other classes, like haloketones, halobenzochinones, other halogenated DBPs and a significant number of non-halogenated DBPs were included as well. The choice of analysed DBPs was also influenced by experimental limitations. The included substances needed to be commercially available as reference standards for quantification (calibration) purposes and the high total number of analysed substances was only manageable by use of multi-analyte methods. Finally, a list of potential DBPs for the analytical experiments was compiled that is presented in Table 9. The table gives basic information of the analytical method used for each substance.

Table 9: DBPs found in the literature and selected for the analytical experiments

Substance name	Analytical method	Measured mass / mass transition	MDL [µg/L]
Trihalomethanes (THMs)			
Trichloromethane	GC-MS	82.9450	0.1
Bromodichloromethan	GC-MS	82.9450	0.1
Dibromochlormethan	GC-MS	128.8920	0.1
Tribromomethane	GC-MS	172.8419	0.1
Dichloroiodomethane	GC-MS	126.9040	0.1
Dibromoiodomethane	GC-MS	170.8440	0.1
Triiodomethane	GC-MS	266.8163	0.1
Chloroiodomethan	GC-MS	175.8883	0.1
Bromochloroiodomethane	GC-MS	174.8806	0.3
Haloacetonitriles (HANs)			
Dichloroacetonitrile	GC-MS	83.9342	0.1
Trichloroacetonitrile	GC-MS	107.9402	0.5
Dibromoacetonitrile	GC-MS	117.9288	0.1
Iodoacetonitrile	GC-MS	166.9224	0.4
Bromochloroacetonitrile	GC-MS	154.8953	0.2
Chloroacetonitrile	GC-MS	74.9870	0.1
Bromoacetonitrile	GC-MS	120.9344	0.1
Haloacetic acids (HAAs)			
Monochloroacetic acid	LC-MS, ES-	92.7→35.0	0.1
Dichloroacetic acid	LC-MS, ES-	126.6→35.0	0.1
Trichloroacetic acid	LC-MS, ES-	160.9→35.0	0.1
Monobromoacetic acid	LC-MS, ES-	137.1→79.0	0.1
Dibromoacetic acid	LC-MS, ES-	216.7→80.4	0.1
Dibromochloroacetic acid	LC-MS, ES-	206.8→79.0	0.1
Bromodichloroacetic acid	LC-MS, ES-	162.9→80.4	0.1
Tribromoacetic acid	LC-MS, ES-	252.5→80.9	0.1
Iodacetic acid	LC-MS, ES-	184.9→127.0	0.1
Bromochloroacetic acid	LC-MS, ES-	172.9 → 81.0	0.1
Other haloacids			
2,2-dichloropropanoic acid/Dalapon	LC-MS, ES-	141.0→35.0	0.1

Substance name	Analytical method	Measured mass / mass transition	MDL [µg/L]
Halonitromethanes (HNMs)			
Trichloronitromethane/Chloropicrin	GC-MS	116.9062	0.1
Dibromonitromethane	GC-MS	172.8419	0.1
Bromonitromethane	GC-MS	92.9335	0.35
Haloketones (HKs)			
1,2-dichloropropanone	GC-MS	78.9759	0.1
1,2-dibromo-3-chloropropane	GC-MS		0.1
1,1,1-trichloropropanone	GC-MS	124.9556	0.7
Halobenzochinones			
2,6-dichloro-1,4-benzoquinone	LC-MS, ES-	177.0→35.0	0.1
2,6-dibromo-1,4-benzoquinone	LC-MS, ES-	266.8→78.9	0.1
Haloacetaldehydes (HALs)			
Trichloroacetaldehyde	GC-MS	81.9373	0.1
Tribromoacetaldehyde	GC-MS	172.8418	0.5
Haloacetamides (HAMs)			
2,2-dichloroacetamide	GC-MS	44.0131	0,5
2,2,2-trichloroacetamide	GC-MS	97.9560	0,5
Other halogenated			
2,6-dibromo-4-nitrophenol	LC-MS, ES-	295.5→80.8	0.1
2,4,6-tribromophenol	LC-MS, ES-	328.7→78.9	0.1
3-bromo-5-chloro-4-hydroxybenzaldehyde	LC-MS, ES-, Der	414.8→80.7	0.1
Tetrachlormethan	GC-MS	116.9060	
1,2-Dibromo-3-chloropropane	GC-MS	154.9258	
Non halogenated			
Phthalimide	LC-MS, ES+	148.1→130.0	0.25
N-cyclohexyl-2-pyrrolidone	LC-MS, ES+	167.9→86.1	0.1
Benzophenone	LC-MS, ES+	182.9→105.0	0.1
Decanal	LC-MS, ES-, Der	335.3→153.0	0.1
Acetaldehyde	LC-MS, ES-, Der	222.8→163.0	0.1
Acetophenon	LC-MS, ES-, Der	299.9→253.8	0.1
4-Nitrobenzoic acid	LC-MS, ES-	165.9→121.8	0.1

Substance name	Analytical method	Measured mass / mass transition	MDL [µg/L]
Salicylic acid	LC-MS, ES-	136.8→93.0	0.1
Propanal	LC-MS, ES-, Der	236.7→151.0	0.1
Benzaldehyde	LC-MS, ES-, Der	284.9→45.9	0.1
Nonenal	LC-MS, ES-, Der	319.0→46.0	0.1
Methylglyoxal	LC-MS, ES-, Der	431.0→137.0	0.1
Dibenzofuran	GC-MS	168.0567	0.1
1-methyl-naphthalene	GC-MS	141.0699	0.1
Inorganic ions			
Bromate	IC		1
Chlorate	IC		10
Chlorite	IC		10

Choice of the active substances for simulations

The choice of biocidal a.s. for the laboratory simulations of disinfection applications considered the results of both literature searches (see chapters 2 & 3). As the analytical experiments were focusing on target analysis of DBPs known from the literature, it was reasonable to choose biocidal a.s. from the substances that were already used in the evaluated literature. However, the analytical experiments also tried to leave the quite narrow selection of biocidal a.s used in the literature and to cover as much of the relevant PTs as possible. For this reason, also a.s. that were not found as often in literature studies were selected.

Sodium hypochlorite is representing the group of biocidal a.s. acting by chlorination used in all of the relevant PTs. Additionally, chlorination is by far the most frequent investigated disinfection method in literature dealing with DBPs. Therefore, sodium hypochlorite was taken as the lead biocidal a.s in the analytical experiments performed within the project. A further biocidal a.s. chosen was sodium hypobromite, as it represents a substance with a high chemical reactivity comparable to hypochlorite and is also the reactive species of several biocidal a.s. currently being within the authorisation process. Oxidation by peroxides is also a reactive principle representing a significant number of biocidal a.s. and found in the literature on DBPs as reactive species. Therefore, hydrogen peroxide was included into the analytical experiments as well. Finally, chloramine T was included, mainly because it is a biocidal a.s. used for disinfection of hard surfaces, a biocidal use which also is subject of the analytical experiments performed in the present project.

Choice of the matrix

As addressed in chapter 3.3, the particular matrix present during a biocidal application is on the one hand not necessarily defined by a particular PT but rather by the particular use. On the other hand, at least when considering a worst-case scenario across the relevant PTs, the matrix will contain organic matter with a comparable content, differing mainly by the ratios of the components (e.g. organic carbon (OC) originating from a plant or an animal source). As the analytical experiments within this project shall cover a wide range of relevant PTs, a detailed focus on different matrices present during particular uses was not reasonable. In contrast, in the analytical experiments it was intended to cover a wide range of TOC concentrations possibly

present during a disinfection process within all relevant PTs. Further criteria for the choice of the matrix components were the reproducibility of the experiments under controlled laboratory conditions and the acceptance with respect to a possible use in a regulatory field. Considering these criteria, guidelines describing efficacy testing of biocidal a.s (EN 14885:2018) were checked. Although the efficacy testing is not related to environmental risk assessment, the efficacy tests are simulating a contamination expected in a disinfection use in a standardised way. The used contamination sources, mainly bovine serum albumin and yeast extract, include a wide range of OC-components and therefore can cover the matrices present during biocidal uses across different PTs. Additionally, to this general matrix one other matrix, specially designed to simulate the contamination in swimming pool water (Kanan et al., 2011), was included. In contrast to the mixtures represented by bovine serum albumin and yeast extract, it includes a number of defined substances, which may influence the DBP formation as well. The original composition of the swimming pool matrix was amended by iodide and bromide sources, as both may be present during a disinfection process and facilitate the formation of brominated or iodinated DBPs. The composition of the matrices used in the simulated disinfection applications is summarised in Table 10 and Table 11.

Table 10: Composition of the general matrix for laboratory disinfection simulations

Ingredient	Ratio (weight based)
Bovine serum albumin	1
Yeast extract	1

Table 11: Composition of the swimming pool matrix for laboratory disinfection simulations

Ingredient	Ratio (weight based)
Urea	30.20
Creatinine	3.75
Uric acid	1.00
Citric acid	1.31
Histidine	2.47
Hipurric acid	3.56
Ammonium chloride	4.08
Sodium phosphate	8.95
Potassium iodide	0.26
Sodium bromide	0.51

6.3 Analytical methods

The samples generated during the simulated disinfection applications and obtained from genuine disinfection uses were analysed by high resolution GC-MS and LC-MS/MS for potential DBPs. The analysed substances and applied methods are given in Table 9, the details of the analytical methods are described in chapters 6.3.1 and 6.3.2. In both cases, GC-MS and LC-MS/MS, the quantitative determination of the analytes was performed using calibration curves set-up using external standards.

6.3.1 Gas chromatography with mass spectrometry coupling (GC-MS)

6.3.1.1 Calibration of GC-MS

Stock solutions for the DBP classes THM, HAN, HK, HAM, HNM, and HAL and EPA 551 Mix were prepared in MTBE with a concentration of 100 µg/mL from the individual DBPs and mixing standards. From these stock solutions, a mixed standard was prepared at 1ug/mL and used for the preparation of the calibration. Due to the possible degradation of DBPs, the stock solution from the individual standards was prepared every 3 months.

For the calibration, 50 mL of MilliQ water were filled into a 60 EPA vial. Afterwards the vials were spiked with the mixing standard (final concentrations: 0.1, 0.2, 1.0, 2.0, 4.0 µg/L) and 10 µl of an internal standard (1,2-dibromopropane; 10 µg/mL) were added. An external calibration was performed, the internal standard was only added to detect losses in the sensitivity of the MS or errors in the injection.

6.3.1.2 Sample preparation for GC-MS measurement

DBPs from EPA method 551 and additional analytes were extracted and analysed using a slightly modified method following Cuthbertson et al. (2020). The method of Cuthbertson et al. (2020) is a modified version of the EPA 551 method and includes representatives of the new DBP classes (HAN, HAM, I-THM, HK). Briefly, 50 mL of the sample was quenched using ammonium chloride and 50 µL of internal standard (1,2-dibromopropane) was added. The pH of the sample was then adjusted to below 1 using concentrated sulfuric acid and 10 g of dried sodium sulfate were added. After the addition of 4 mL MTBE, the sample was shaken for 5 min and the organic phase was separated and transferred to a vial without headspace. Analysis of 25 DBPs was carried out on a Q Exactive GC Orbitrap GC-MS/MS from Thermo Scientific™ (Bremen, Germany) coupled to a TRACE™ 1310 gas chromatograph and TriPlus™ RSH autosampler from Thermo Scientific™ (Bremen, Germany). Instrumental conditions applied for GC analysis in this study are summatised below:

Chromatographic System:	Thermo Fisher Scientific Trace 1310 GC		
Analytical Column	Rxi-5Sil-MS (60 m, 0.25 mm i.d., 0.25 µm film)		
Inlet	PTV Splitless, 40°C		
Injection Volume	1 µl		
Carrier gas	He		
Gradient	Time [min]	Temperature [°C]	Rate [°C/min]
	0.0	35	0
	8.0	35	0
	8.0→26.3	35→200	9
	26.3→29.1	200→270	25
	30.1	270	0
Detection System	Thermo Fisher Scientific Q Exactive		
MS Scan mode	Emission current: 50 Ma		
	Electron energy: 70 eV		
	MS1 resolution: 60000		
	Mass range: 50-600 m/z		

6.3.2 Liquid chromatography with mass spectrometry coupling (LC-MS/MS)

The analysis by LC-MS/MS was performed by three different analytical methods. The methods are based on a method for the analysis of HAAs described in an application note from Sciex (Hoon, 2019) The implementation of two different methods is considering the optimal ionisation mode (ES+ and ES-) for the observed analytes. The third method was used for analysis of carbonyl compounds, which could by analysed sensitive enough only after derivatisation with dinitrophenylhydrazine (DNPH, see chapter 6.3.2.2). The assignment of the substances analysed by LC-MS/MS to the three methods is summarised in Table 12.

Table 12: Assignment of analysed substances to the different LC-MS/MS analytical methods

ES+ analyte mix	ES- analyte mix	ES- analyte mix after dervatisation
Phthalimide, N-cyclohyexyl-2-pyrrolidone, Benzophenone	Monochloroacetic acid, Dichloroacetic acid, Trichloroacetic acid, Monobromoacetic acid, DIbromoacetic acid, Dibromochloracetic acid, Bromodichloroacetic acid, Tribromoacetic acid, 2,2-dichloropropanoic acid, Iodacetic acid, Bromochloracetic acid, 2,6 dichloro-1,4-benzoquinone, 2,6-dibromo-1,4 benzoquinone, 2,6-dibromo-4-nitrophenol, 2,4,6-Tribromophenol, 4-Nitrobenzoic acid, Salicylic acid	3-bromo-5chloro-4-hydroxybenzaldehyd, Propanal, Decanal, Acetaldehyde, Benzaldehyde, Nonenal, Acetophenon

Details for the three applied LC-MS/MS methods are below:

Instrumentation and conditions for LC-MS analysis ES+ analyte mix

Chromatographic System:	Agilent (1290 HSP, Multisampler, MCT)		
Analytical Column	Synergi Hydro RP 150 x 2.0 mm, 4.0 µm		
Column Temperature	55°C		
Injection Volume	10 µl		
Mobile Phase A	Water + 0.1 % acetic acid		
Mobile Phase B	Acetonitrile + 0.2 % acetic acid		
Flow rate	0.5 mL/min		
Gradient	Time [min]	Phase A [%]	Phase B [%]
	0.0	80	20
	0.5	80	20
	2.5	0	100
	5.0	0	100
	5.1	80	20
	7.0	80	20
Divert Valve	no		
Detection System	Sciex Q TRAP 5500		
Ionisation	Electro Spray (ESI+)		

Instrumentation and conditions for LC-MS analysis of ES- mix

Chromatographic System:	Agilent (1290 HSP, Multisampler, MCT)		
Analytical Column	Synergi Hydro RP 150 x 2.0 mm, 4.0 µm		
Column Temperature	55°C		
Injection Volume	10 µl		
Mobile Phase A	Water + 0.1 % acetic acid		
Mobile Phase B	Acetonitrile + 0.2 % acetic acid		
Flow rate	0.5 mL/min		
Gradient	Time [min]	Phase A [%]	Phase B [%]
	0.0	99.5	0.5
	1.5	99.5	0.5
	5.0	2	98
	8.0	2	98
	8.1	99.5	0.5
	10.0	99.5	0.5
Divert Valve	no		
Detection System	Sciex Q TRAP 5500		
Ionisation	Electro Spray (ESI-)		

Instrumentation and conditions for LC-MS analysis ES- analyte mix after derivatisation

Chromatographic System:	Agilent (1290 HSP, Multisampler, MCT)		
Analytical Column	Synergi Hydro RP 150 x 2.0 mm, 4.0 µm		
Column Temperature	55°C		
Injection Volume	10 µl		
Mobile Phase A	Water + 0.2 % acetic acid		
Mobile Phase B	Acetonitrile (2mM ammonium acetate) + 0.2 % acetic acid		
Flow rate	0.5 mL/min		
Gradient	Time [min]	Phase A [%]	Phase B [%]
	0.0	80	20
	0.5	80	20
	2.5	0	100
	5.0	0	100
	5.1	80	20
	7.0	80	20
Divert Valve	no		
Detection System	Sciex Q TRAP 5500		
Ionisation	Electro Spray (ESI-)		

6.3.2.1 Calibration of LC-MS/MS

Stock solutions of the analysed substances were prepared at nominal concentrations of 1.18 to 6.33 mg/mL in methanol by precisely weighing and solving the substances in 10 mL volumetric flasks. Using the stock solutions, substance mixes according to the applied analytical method (see Table 12) were prepared at a concentration of 10 µg/mL for each substance. The

substances of ES+ and ES- analyte mix were diluted in methanol and the substances of the ES- analyte mix with analytes for derivatisation was diluted in acetonitrile.

ES+ and ES- analyte mix: The 10 µg/mL mixes were combined and further diluted with methanol:water (1:1) to give a final analyte mixture with a concentration of 10 ng/mL. Using this solution ten calibration samples were prepared in a concentration range of 0.1 – 10 ng/mL in methanol:water (1:1).

ES- analyte mix with analytes for derivatisation: The 10 µg/mL mix was further diluted with acetonitrile + 0.5% acetic acid to a concentration of 20 ng/mL. Using this solution ten calibration samples were prepared in a concentration range of 0.1 – 10 ng/mL in acetonitrile:water (1:1) + 0.5% acetic acid. 1 mL of the mixture was treated with 5 µL of a 3 mg/mL Dinitrophenylhydrazine (DNPH) solution in acetonitrile. The derivatisation reaction was performed at 60°C for 2 hours in a drying oven.

6.3.2.2 Sample preparation for LC-MS/MS measurement

ES+ and ES- analyte mix: For LC-MS/MS analysis 500 µL of a sample was mixed with 500 µL methanol. Samples were further diluted in order to match the calibration range, if necessary. The final solvent composition was always methanol:water (1:1).

ES- analyte mix with analytes for derivatisation: The aqueous samples were ultra-sonicated for 15 min. For the derivatisation 0.5 mL of a sample was mixed with 0.5 mL acetonitrile + 1% acetic acid. Samples were further diluted using acetonitrile:water + 0.5% acetic acid in order to match the calibration range, if necessary. Subsequently, 1 mL of the final sample was treated with 5 µL of a 3 mg/mL Dinitrophenylhydrazine (DNPH) solution in acetonitrile. The derivatisation reaction was performed at 60°C for 2 hours in a drying oven. Afterwards the samples were analysed by LC-MS/MS.

6.3.3 Other analytical methods

Inorganic anions

For the analysis of the anions chlorite, chlorate and bromate, a measurement was carried out using an ion chromatography (IC). For this, about 10 mL of the sample volume of each sample was quenched and kept for measurement. About 5 mL of each sample was transferred to an IC sample vial and sealed. Afterwards an analysis in an ion chromatograph followed. The ion chromatographic system used was a Metrohm 930 Compact IC Flex (METROHM AG, 2022) with a combination of CO_2 suppression (MCS) and chemical suppression and a Metrohm 732 conductivity detector according to DIN EN ISO 10304-1. The analytical column for anion separation was a Metrosep A Supp 7 universal anion column (4.0 mm × 250 mm) at an injection volume of 50 µL. For an assessable analysis of the three compounds considered, several different dilutions were necessary to keep the measurement within the calibration range.

Active chlorine

Free chlorine was measured photometrically using the DPD method. The test kit from HACH (method 10069) was used for measurement according to the specifications.

Active bromine

Bromine was measured photometrically using the DPD method. The test kit from HACH (method 8016) was used for measurement according to the specifications.

Hydrogen peroxide

H_2O_2 was measured photometrically at 400 nm by adding 2 mL sample and 0.2 mL of potassium titanium oxide oxalate solution (50 g/L) with the TiO-Ox Colorimetric Assay (Chhetri et al., 2020)

pH and TOC

TOC and pH were analysed immediately after sampling according to DIN, EN, or ISO standard protocols. The pH was measured using a sensION MM374 Hach Lange instrument according to DIN 10523 (DIN. 2009). Total organic carbon (TOC) was analysed via combustion using a Shimadzu carbon/nitrogen analyser (TOC-L (LCPH)) according to DIN 1484 (DIN, 2019).

6.4 Experimental procedures

6.4.1 Design of the laboratory simulations

The formation of DBPs is influenced by different factors of a particular biocidal application and the broad range of relevant parameters cannot be covered by a limited number of laboratory experiments. However, the presence or absence of water as a solvent (reaction medium) is assumed to be an important parameter with respect to DBP formation potential. Focusing on this, biocidal applications can be roughly divided into two general groups: i) applications in aqueous solution, and ii) applications on (hard) surfaces and absence of water. In the second case it needs to be specified that small amounts of water may be present in the formulation of the biocidal a.s., but still the reaction conditions will be significantly differing from an aqueous solution. Following this consideration two experimental set-ups were designed for the laboratory simulations. For both set-ups, the laboratory experiments aim to investigate worst-case conditions with respect to DBP formation. Therefore, in both set-ups basic reaction parameters, e.g. temperature or biocidal a.s. concentration were varied. An overview on the laboratory experiments performed within the present study is given in Table 13, the experimental details are described in the following chapters.

Table 13: General set up of the laboratory simulations

Biocidal active substance	Simulation set up	Varied parameters
Hypochlorite	Aqueous swimming pool matrix	Conc. a.s.; Conc. TOC; Temp.; t (kinetic experiment)
Hypobromite	Aqueous swimming pool matrix	Conc. a.s.; Conc. TOC; Temp.; t (kinetic experiment)
Hypochlorite	Aqueous general matrix	Conc. a.s.; Conc. TOC; Temp.; pH; t (kinetic experiment)
Hydrogen peroxide	Aqueous general matrix	Conc. a.s.; Conc. TOC; Temp.; pH; t (kinetic experiment)
Hypochlorite	General matrix on hard surface	Conc. a.s.; Conc. TOC; t (kinetic experiment)
Chloramine T	General matrix on hard surface	Conc. a.s.; Conc. TOC; t (kinetic experiment)

6.4.1.1 Laboratory simulations in aqueous solution

Laboratory simulations in aqueous solution cover a main part of biocidal uses in PT2 like swimming pool water or wastewater treatment and the most biocidal uses in PT5, PT11 and

PT12. As described in chapter 6.2 for the simulations in aqueous solution two matrices, a general one and one focusing on matrix loading present in swimming pool water are applied.

General experimental procedure

The simulations in aqueous solution were performed in screw capped laboratory glass flasks (300 mL volume for subsequent LC-MS/MS analysis and 1000 mL volume for subsequent GC-MS analysis). Appropriate volumes of aqueous matrix stock solutions (TOC 1-10 mg/L depending on particular stock solution), aqueous stock solution of potassium iodide (swimming pool matrix only) and sodium bromide (swimming pool matrix only) as well as aqueous buffer solution were filled into the flasks. The vessels were filled with ultrapure water up to approx. 50 mL below the maximum volume. The pH value was determined and adjusted (±0.05), if necessary. Afterwards an aqueous stock solution of the biocidal a.s. was added and the vessel volume completely filled up with ultrapure water (no headspace present during incubation). The samples were incubated at constant and controlled temperature. Incubation time was either 24h (standard) or within the range of 0-6h (kinetic experiment). At sampling time point a defined volume was removed for determination of residual biocidal a.s. and pH value. The remaining sample volume was treated with a quenching reagent. Afterwards subsamples in duplicate were worked-up and analysed as described in chapters 6.3.1.2 (GC-MS) and 6.3.2.2 (LC-MS/MS). The detailed set-up of the performed laboratory simulations in aqueous solution are summarised in Table 14 (swimming pool matrix) and Table 15 (general matrix).

Table 14: Conditions of laboratory simulations performed with swimming pool matrix

Biocidal a.s.	TOC conc. in matrix [mg/L]	Biocidal a.s. conc. [mg/L]	Incubation temperature [°C]	pH	Incubation time [h]	Varied parameter
Hypochlorite	0.1	50	30	7	24	TOC conc.
Hypochlorite	1	50	30	7	24	TOC conc.
Hypochlorite	10	50	30	7	24	TOC conc.
Hypochlorite	1	10	30	7	24	Biocidal a.s. conc.
Hypochlorite	1	100	30	7	24	Biocidal a.s. conc.
Hypochlorite	1	50	15	7	24	Temp.
Hypochlorite	1	50	45	7	24	Temp.
Hypochlorite	1	50	30	7	0, 1, 3, 4, 5, 6	Time
Hypobromite	0.1	100	30	7	24	TOC conc.
Hypobromite	1	100	30	7	24	TOC conc.
Hypobromite	10	100	30	7	24	TOC conc.
Hypobromite	1	20	30	7	24	Biocidal a.s. conc.
Hypobromite	1	200	30	7	24	Biocidal a.s. conc.

Biocidal a.s.	TOC conc. in matrix [mg/L]	Biocidal a.s. conc. [mg/L]	Incubation temperature [°C]	pH	Incubation time [h]	Varied parameter
Hypobromite	1	100	15	7	24	Temp.
Hypobromite	1	100	45	7	24	Temp.
Hypobromite	1	100	30	7	0, 1, 3, 4, 5, 6	Time

Table 15: Conditions of laboratory simulations performed with general matrix in aqueous solution

Biocidal a.s.	TOC conc. in matrix [mg/L]	Biocidal a.s. conc. [mg/L]	Incubation temperature [°C]	pH	Incubation time [h]	Varied parameter
Hypochlorite	0.1	50	30	7	24	TOC conc.
Hypochlorite	1	50	30	7	24	TOC conc.
Hypochlorite	10	50	30	7	24	TOC conc.
Hypochlorite	1	10	30	7	24	Biocidal a.s. conc.
Hypochlorite	1	100	30	7	24	Biocidal a.s. conc.
Hypochlorite	1	50	15	7	24	Temp.
Hypochlorite	1	50	45	7	24	Temp.
Hypochlorite	1	50	30	4	24	pH
Hypochlorite	1	50	30	9	24	pH
Hypochlorite	1	50	30	7	0, 1, 3, 4, 5, 6	Time
Hydrogen peroxide	0.1	50	30	7	24	TOC conc.
Hydrogen peroxide	1	50	30	7	24	TOC conc.
Hydrogen peroxide	10	50	30	7	24	TOC conc.
Hydrogen peroxide	1	10	30	7	24	Biocidal a.s. conc.*
Hydrogen peroxide	1	100	30	7	24	Biocidal a.s. conc.*
Hydrogen peroxide	1	50	15	7	24	Temp.*
Hydrogen peroxide	1	50	45	7	24	Temp.*

Biocidal a.s.	TOC conc. in matrix [mg/L]	Biocidal a.s. conc. [mg/L]	Incubation temperature [°C]	pH	Incubation time [h]	Varied parameter
Hydrogen peroxide	1	50	30	4	24	pH*
Hydrogen peroxide	1	50	30	9	24	pH*
Hydrogen peroxide	1	50	30	7	0, 1, 3, 4, 5, 6	Time*

* Analysis of simulation samples only by LC-MS/MS

6.4.1.2 Laboratory simulations on hard surfaces

Laboratory simulations on hard surfaces cover biocidal uses of PT2 and a main part of biocidal uses in PT3 and PT4. Although not fitting optimally, also biocidal uses of PT1 could considered as covered at least with respect to the idea that by the performed laboratory simulations on hard surfaces biocidal uses are simulated which take place in absence of water. For the simulations on hard surfaces the general matrix was applied. No similar experiments have been found in literature, the experimental set-up had to be designed from scratch for this reason.

General experimental procedure

The simulations on hard surfaces were performed in stainless steel vessels with a surface area of 78 cm^2 and a height of 6.5 cm (Figure 5). The vessels were equipped with a gas tight sealed top cover. The fitting on the top cover was closed by a rubber septum enabling the injection of a solvent without opening the vessel.

Figure 5: Vessel (left) and top cover (right) used for laboratory simulations on hard surfaces

Source: own illustration, picture of incubation vessel and top cover

The aqueous matrix stock solutions were further diluted and 975 µL were pipetted on the bottom of the vessel (TOC: 2.5µg/cm^2, 25µg/cm^2 or 80µg/cm^2). The bottom of the vessel was evenly coated by the solution and dried overnight. Prior to application of the biocidal a.s., the test vessel was closed and pre-tempered at 30°C for 20 min. Afterwards, an aqueous stock solution of the biocidal a.s. was added through the rubber septum diluted in 1 mL water and distributed evenly on the bottom of the vessel. The samples were incubated at 30°C. Incubation time was either 120 min (standard) or within the range of 0-120 min (kinetic experiment). At

sampling time point, 30 mL water with quenching reagent were added and the bottom of the vessel rinsed thoroughly. Afterwards subsamples in duplicate were worked-up and analysed as described in chapters 6.3.1.2 (GC-MS) and 6.3.2.2 (LC-MS/MS). The pH value of the water was determined. The detailed set-up of the performed laboratory simulations in aqueous solution are summarised in Table 16.

Table 16: Conditions of laboratory simulations performed with general matrix on hard surfaces

Biocidal a.s.	TOC conc. in matrix [µg/cm²]	Biocidal a.s. conc. in applied volume [g/L]	Incubation temperature [°C]	pH	Incubation time [min]	Varied parameter
Hypochlorite	2.5	5	30	7	120	TOC conc.
Hypochlorite	25	5	30	7	120	TOC conc.
Hypochlorite	80	5	30	7	120	TOC conc.*
Hypochlorite	25	0.5	30	7	120	Biocidal a.s. conc.
Hypochlorite	25	10	30	7	120	Biocidal a.s. conc.
Hypochlorite	25	5	30	7	0, 20, 40, 60, 80, 100, 120	Time
Chloramine T	2.5	25	30	7	120	TOC conc.
Chloramine T	25	25	30	7	120	TOC conc.
Chloramine T	80	25	30	7	120	TOC conc.*
Chloramine T	25	2.5	30	7	120	Biocidal a.s. conc.
Chloramine T	25	50	30	7	120	Biocidal a.s. conc.
Hydrogen peroxide	1	50	30	7	0, 20, 40, 60, 80, 100, 120	Time

* Analysis of simulation samples only by LC-MS/MS

6.4.2 Analytical control experiments

The laboratory simulations of disinfection application as discussed in chapters 6.6.2 - 6.6.4 delivered partially unexpected results (e.g. either very high or no difference between DBP concentrations for certain parameter variations; no time dependence of formed DBP amounts) especially for the DBPs quantified by LC-MS/MS. In order to elucidate possible reasons for the observed results several control experiments were performed.

6.4.2.1 Reproducibility of laboratory simulations

Control experiments to check the reproducibility of laboratory simulations in aqueous solution were performed for the DBPs quantified by LC-MS/MS. Both matrices and the three corresponding biocidal a.s. were considered. For each matrix and biocidal a.s. combination, one set of reaction parameters was chosen and the laboratory simulation was performed with five

individual replicates. The detailed setup of the control experiments for reproducibility is summarised in Table 17. The experiments were conducted as described in chapter 6.4.1.1 and subsamples in duplicate were worked-up and analysed as described in chapter 6.3.2.2.

Table 17: Conditions of reproducibility experiments for laboratory simulations in aqueous solution

Biocidal a.s.	Matrix	TOC conc. in matrix [mg/L]	Biocidal a.s. conc. [mg/L]	Incubation temperature [°C]	pH	Incubation time [h]
Hypochlorite	swimming pool	1	50	30	7	24
Hypobromite	swimming pool	1	100	30	7	24
Hypochlorite	general	1	50	30	7	24
Hydrogen peroxide	general	1	50	30	7	24

6.4.2.2 DBP background concentrations

Control experiments to determine possible background concentrations of DBPs in the a.s. application solutions as used for the laboratory simulations were performed for the DBPs quantified by LC-MS/MS. Aqueous application solutions of hypochlorite and hypobromite were applied into ultrapure water at concentrations of 50 mg/L (active chlorine) and 100 mg/L (bromine). Final sample volume was 300 mL. For chloramine T control of background values was performed in a final volume of 30 mL, as used for in disinfection simulations on surfaces. For comparison of the background values of all a.i. the results were divided by factor 10 showing the values as they will result using a 300 mL sample volume. Assuming a sample volume of 300 mL, the chloramine T concentration was 166 mg/L. The sample volume was treated with the quenching reagent. Afterwards subsamples in duplicate were worked-up and analysed as described in chapters 6.3.1.2 (GC-MS) and 6.3.2.2 (LC-MS/MS). Background concentrations originating from the matrices applied in the simulations, swimming pool matrix and general matrix, were investigated by preparing 300 mL simulation test solutions at TOC concentrations of 10 mg/L as used for disinfection simulations at high TOC concentration. Subsamples in duplicate were worked-up and analysed as described in chapters 6.3.1.2 (GC-MS) and 6.3.2.2 (LC-MS/MS) without previous application of an a.s..

6.4.3 Samples from genuine disinfection applications

Additional to the laboratory simulations, samples originating from genuine disinfection uses were analysed for DPBs considered in the present project. The samples were obtained from an open-air swimming pool and a thermal spa, both representing uses in PT2 and from several industrial cooling systems representing uses in PT11.

6.4.3.1 Samples from open air swimming pool and thermal spa

Water samples from the open-air swimming pools were collected by RWTH-Aachen University in 1 L amber glass bottles without headspace and as duplicates. Three different open-air pools and seven pools in the thermal spa were sampled together with the corresponding filling water. The samples were taken at a time when a large number of swimmers were expected. All samples were spiked with 2 mg/L ammonium chloride for analysis by GC-MS, except for nitrosamine analysis, which was quenched with sodium sulfite and ascorbic acid as a quenching agent for

analysis by LC-MS/MS. Samples were stored at 4 °C and extracted within 7 days. All analyses were carried out as duplicates and the mean value of both analyses was given as the measured value.

6.4.3.2 Samples from industrial cooling systems

Water samples from the industrial cooling were collected by a company providing disinfection services for industrial facilities. Sampling was performed mostly in duplicate in 1 L amber glass bottles without headspace. A total of 16 cooling systems were sampled at 10 different facilities. The samples were immediately stored in a polystyrene box equipped with cold packs and shipped to the laboratory. A laboratory site the samples were stored at 4 °C and extracted within 7 days.

6.5 Data evaluation

6.5.1 General calculation

Calculations were performed by means of Microsoft Excel software using up to fifteen decimal points. In this report, numerical values are rounded to a smaller degree of precision (number of digits) than used in the actual calculation. Minor differences in results obtained from calculations with such rounded values in comparison to those obtained with higher precision values are possible. They are, however, well within the limits of the experimental accuracy and thus of no practical concern.

6.5.2 Calculation of the DPB concentrations

DPB concentrations measured with GC/MS and LC-MS/MS based on the performed calibration, were converted into concentration values in the test samples considering dilution factors occurred during sample work-up. Data evaluation was performed with Microsoft Excel software. Concentration values smaller than the limit of detection were assigned as <LOD and if not detected as n.d..

6.6 Results and discussion

Results of the DBP analyses obtained in the analytical control experiments, the laboratory disinfection simulations and determined in samples from genuine disinfection applications are presented and discussed in the following chapters. The detailed analytical results of the laboratory disinfection simulations were sorted by the applied matrix and a.s.. Furthermore, for all measurements, laboratory simulations and genuine disinfection samples, individual tables were prepared for GC-MS and LC-MS/MS measurements. In the tables of the laboratory simulations, the results originating from variation of a given reaction parameter were arranged next to each other. Result columns that are relevant for different reaction parameter variations are doubled in the tables to provide a better overview. Furthermore, separate tables were prepared for the variation of time as reaction parameter (kinetic experiments). The determined DBPs are sorted by the DBP classes: THM (Trihalomethanes), I-THM (Iodo-Trihalomethanes), HNM (Halonitromethanes), HAL (Haloacetaldehydes), HAN (Haloacetonitriles), HAM (Haloacetamides), HK (Haloketones), HAA (Haloacetic acids), other haloacids, HBQ (Halobenzochinones), other halogenated and non-halogenated, the latter mostly containing non-halogenated aldehydes and ketones. Main results were additionally visualised in figures corresponding to the values in the tables.

6.6.1 Analytical control experiments

Due to unexpected and not easily interpretable analytical results, especially for the analysis with LC-MS/MS, control measurements were performed to check the analytical method and to find an explanation for the observed results. The control experiments encompassed test for background concentrations of the DBPs analysed by LC-MS/MS (chapter 6.6.1.1) and the reproducibility of the results for disinfection simulations in solution (chapter 6.6.1.2).

6.6.1.1 Background concentrations from matrices and application solutions

Background concentrations were determined separately in dissolved matrix solutions and application solutions mixed with quenching reagent. The results are summarized in Table 32 (Annex D). It should be pointed out, that detected background values do not necessarily show the presence of the particular analyte in the sample. Such results may also origin from a disturbing signal fulfilling the MS detection parameters of the particular analyte. In both matrices, the highest TOC concentration applied in the disinfection simulations was used for the control measurements. For most of the analysed DBPs no background concentrations were determined in the matrix solutions. In the swimming pool matrix, the HAAs MCAA and MBAA and acetophenone are detected in the range of 1 µg/L. Acetaldehyde was found only at small concentration in the range of the detection limit but a quite high value of 12 µg/L was found for propanal. Similar results were obtained for the general matrix: MBAA and acetophenone were detected in the range of 1 µg/L, however neither MCAA nor propanal were found. Instead, benzaldehyde was found in the range of 0.5 µg/L and a quite high amount of 21 µg/L acetaldehyde.

The background values in the applied a.s. were detected at medium a.s. concentrations of 50 mg/L (active chlorine) and 100 mg/L (bromine) with respect to the performed simulations and the DBP background values in chloramine T were recalculated to a sample volume of 300 mL to be comparable to the values of the other a.s.. The corresponding chloramine T concentration was 166 mg/L. As the control experiments were performed with the a.s. and the quenching reagent at least for hypochlorite and chloramine T, with ascorbic acid as quenching reagent, it is possible that the DBP background is resulting from reaction of the both. Considering a reaction between hypochlorite or chloramine T with ascorbic acid, the performed control experiments represent a worst-case scenario, as a.s. was present at initial and thus much higher concentration as at the end of simulation experiment. Similar as for the matrices, no background was detected for the majority of analysed DBPs. In samples with hypochlorite, DCAA and TCAA were detected in the range of 6 µg/L and 2,6-dichloro-1,4-benzoquinone was detected below 2 µg/L. In samples with chloramine T, MCAA, DCAA and TCAA were detected at low levels. The occurrence of chlorinated DBPs in the background of the two a.s. is reasonable as well as the brominated DBPs found as background in the hypobromite samples with TBAA in a significant range of 7 µg/L. Extraordinary is the value of 126 µg/L for 2,4,6-tribromophenol. It was found only at much lower values in the simulation experiments. However, in a kinetic simulations experiment "failed" because the pH was not properly buffered and determined to be approx. pH3, 40 µg/L 2,4,6-tribromophenol are found for the 0h value. Therefore, the high amount found as background seems not necessarily to be an outlier.

Regarding the concentration ranges of the main DBPs detected within the disinfection simulations, the measured background concentrations did not significantly falsify the obtained results. Most significantly affected were the simulations with hydrogen peroxide in general matrix. For these simulations it cannot be excluded that the detected acetaldehyde concentrations were originating from the matrix background only. Furthermore, background concentrations determined in the a.s. applied in the simulations can be also expected in

formulated commercial disinfection products which will contribute to the total amount of DBPs generated within a disinfection procedure. These DBPs are of course independent of the particular matrix present during the disinfection but will depend on the particular a.s. and perhaps on further ingredients of the formulated disinfection product. The detected background concentrations were in several cases not reproduced in the disinfection simulations. This observation once again indicates the dynamic chemical reactions in case a reactive a.s. (hypochlorite and hypobromite). Background DBPs are potentially reacting further to form other DBPs.

6.6.1.2 Reproducibility of laboratory simulations

Five separate replicates for disinfection simulations in solutions were prepared for each a.s./matrix combination to test the reproducibility of the disinfection simulation set-up. The experimental parameters were corresponding to one set of parameters already applied in previous experiments and are summarized in Table 21. The experimental performance followed the same protocol as used for previous experiments and the results are summarised in Table 33 - Table 36 (Annex D). The tables also include the results of the original simulation experiment at with corresponding experimental parameters. Although not valid for all single results, a general observation is possible for all a.s./matrix combination. The concentrations detected for particular DBPs in the five replicates of the reproducibility samples were in good agreement, indicating that both experimental and analytical reproducibility were mostly given for exact the same reaction conditions. However, in several cases these results were differing from the results of the original simulation experiment. The observed differences were not contradicting the original results as mostly the same DBPs or DBPs from same classes were found but at partially significantly differing concentrations. The results show that with the applied experimental set-up it was not possible to adequately control the disinfection simulations. Obviously relevant experimental parameters significantly influencing the result with respect to generation of DBPs were out of scope and not controlled adequately. Regarding the complex reaction mixture, including a high number of possible DBPs, which only a part of is within the analytical scope of the present study and interim products further reacting with the a.s., the matrix or with each other, it seems possible that slight changes of reaction parameters may had a significant impact on the result of the simulations. Consequently reproducibility, especially considering not only parallel replicates but also independently prepared experiments on different time points (and by different laboratories), was a serious issue.

Reproducibility for hypochlorite in artificial swimming pool matrix

Compared to the original experiment, the total amount of formed DBPs was higher in the reproducibility experiments and this was mainly due to the higher amounts of the HAAs DCAA and BCAA, which increased approx. by factor 25 and 10, respectively. At the same time MCAA, not observed in the original experiment, was detected at low levels and interestingly TCAA was detected at approx. half of the original concentration. In sum, a lower chlorination degree of the HAAs was observed. The amount of brominated HAAs increased, mostly due to high BCAA concentrations but also BDCAA was observed at higher concentrations and at the same time DBCAA at lower ones. Besides the changes within HAAs, propanal, not observed in the original experiment was detected but benzaldehyde, originally observed at similar concentration not detected any more. The overall observation was, that more or less the same chemical reactions occur in the original simulation and the reproducibility experiments but the outcome with respect to analysed DBPs was different.

Reproducibility for hypobromite in artificial swimming pool matrix

The differences between original simulation and reproducibility experiments with hypobromite were less numerous compared to hypochlorite. Most noticeable was the significantly higher concentration of DBAA in the reproducibility experiments. Regarding the simulation experiments at all three hypobromite concentrations, the results of the reproducibility experiments were better fitting in as the original simulation applied with 100 mg/L hypobromite, where the DBAA amount was unexpectedly low. DCAA and TCAA observed in Rep 4 of the reproducibility experiments were clearly accounted as an analytical issue, most probable a contamination, as both were only detected in one of two replicates samples of this simulation vessel. Interestingly propanal, identified as background in the swimming pool matrix and detected at these concentrations in the original simulation using 100 mg/L hypobromite was not detected any more. However, the propanal concentration was differing in the original simulations and depending on varied reaction parameters.

Reproducibility for hypochlorite in general matrix

Like in the reproducibility experiments for hypochlorite in swimming pool matrix, lower chlorination degree of the HAAs was observed, but significantly less pronounced. Observed MCAA and DCAA concentrations were higher and at the same time the TCAA concentration was lower. Also noticeable were the results of the brominated HAAs, where exceptionally significant differences were observed between the replicates of the reproducibility experiments. In the original simulation experiments, brominated HAAs and THMs were found at low amounts, HAAs only in the kinetic experiments. In the reproducibility experiments, especially BDCAA and BCAA were always detected and in three of five replicates the concentrations were significantly higher, ranging between 15 µg/L and 30 µg/L. The higher amounts of BDCAA and BCAA did not seem to be random, as either BDCAA and BCAA were both observed at higher concentrations or were both at low concentrations in a particular simulation vessel and the two replicate analytical samples measured for each simulation vessel were always in good agreement. However, significant differences between the five replicates could not be easily explained as the responsible parameter was obviously not identified.

Reproducibility for hydrogen peroxide in general matrix

Similar as in the original simulation, in the reproducibility experiments a few aldehydes were detected as DBPs, but the amounts are even lower. Propanal was not found in the reproducibility experiments, while the amounts of benzaldehyde were slightly higher. The detection of decanal in one replicate of the reproducibility experiments seems random and was assumed to be an analytical issue and the increased amounts of acetaldehyde may origin from the background observed in the general matrix. The background was also assumed to be the reason for MBAA found at low amounts in three of five replicates.

6.6.2 Laboratory simulations with swimming pool matrix

Treatment of the swimming pool matrix with chlorine led to the formation of a high number of different DBPs, as summarized in Table 37, Table 38 and Table 39, as well as in Table 40 for the kinetic experiments. Substances from the most DPB classes were detected. The reason for this high number of formed DBPs is the high reactivity of chlorine, leading to corresponding high number of unspecific reactions with the matrix components. As also observed in other studies (Richardson et al., 2010), THMs and HAAs were the dominant DBP classes with respect to the generated amounts. The highest amounts of THMs and HAAs were 66.3 µg/L and 52.9 µg/L, both observed at highest chlorine concentration (100 mg/L). Within the two DBP classes highest amounts of single DBP were determined for the trichlorinated representatives trichloromethane (21.1 µg/L) and trichloroacetic acid (19.4 µg/L). The dominant formation of the trichlorinated substances at high chlorine concentration was expectable. However, also brominated and

iodinated DBP were detected. This indicates that the presence of bromide and iodide in the matrix led to an in-situ formation of bromine and iodine, which subsequently reacted with organic matter of the matrix. Alternatively, brominated and iodinated DBP could be formed by substitution reactions after an initial formation of chlorinated DBP (Westerhoff et al., 2004).

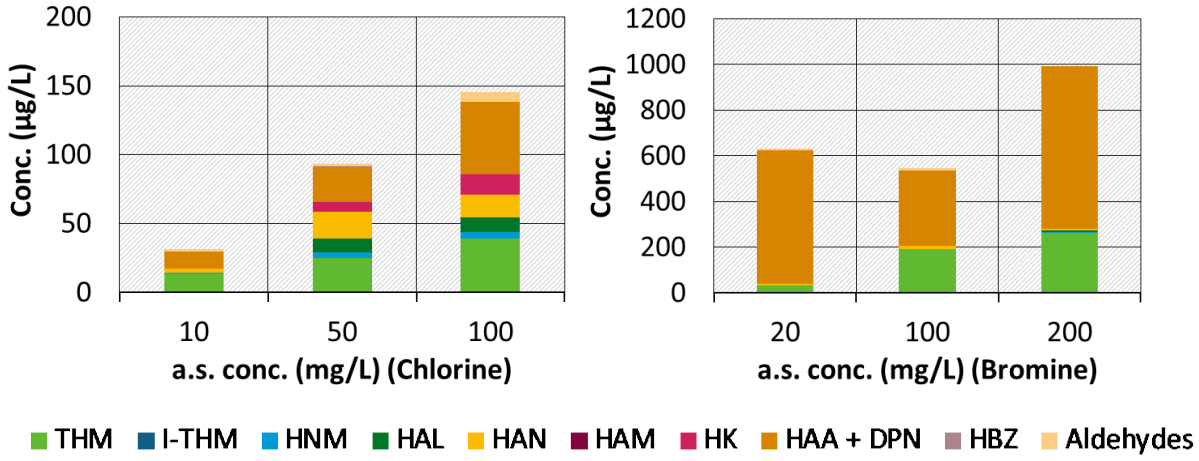
The number of different DBPs determined after treatment of the swimming pool matrix with bromine was significantly reduced compared to chlorine as a.s.. The higher reactivity of chlorine compared to bromine led to more different reactions occurred in presence of chlorine and as consequence a higher number of formed DBPs. As expected mainly brominated DBPs were found. The results are summarised in Table 41, Table 42 and Table 43, Table 44 for the kinetic experiments. Chlorinated and iodinated DBP were also formed, although only at significantly lower concentrations. The total concentration of formed DPBs was higher after the treatment with bromine compared to chlorine. The reason was the faster reaction of bromine compared to chlorine. The main reactive species are the protonated hypochlorous and hypobromous acids (HOCl and HOBr), the deprotonated anions (OCl^- and OBr^-) are significantly less reactive. At pH 7 almost only HOBr is present, while HOCl:OCl^- are present at a ratio of 3:1 (Brugger, 2014). This led to a faster reaction of bromine and a higher amount of the corresponding DBPs. Highest concentrations of THMs (186 µg/L) and HAAs (5484 µg/L) were determined in simulations with high TOC concentration. However, the concentration of HAAs was exceptionally high in this case and an analytical issue is suspected to be the reason. Generally, the total amount of formed DBPs was dominated by three substances: the THM tribromomethane and the HAAs dibromoacetic acid and tribromoacetic acid. The three DBP were, depending on the varied parameter, mostly found in a concentration range of approx. 50 - 500 µg/L (excluding the exceptionally high values mentioned before), while the concentrations of most other formed DBPs never exceeded 10 µg/L. Highest determined concentrations of tribromomethane, dibromoacetic acid and tribromoacetic acid were 183 µg/L, 470 µg/L (2245 µg/L questionable result) and 343 µg/L (3233 µg/L questionable result). The occurrence of iodinated DBPs couldbe, like in case of simulations with chlorine, explained by in-situ formation of iodine. However, bromine should not oxidize chloride to chlorine. Therefore, the chlorinated DBPs are supposed to be generated via substitution reactions (Westerhoff et al., 2004). For both a.s., chlorine and bromine, non-halogenated DBPs generated by oxidation reactions (aldehydes and ketones) were observed at similar concentrations.

Variation of the chlorine and bromine concentrations

The influence of the a.s. concentration was investigated using three different chlorine and bromine concentrations. Figure 6 shows the total amount of DBPs generated and analysed. The DBP amount after treatment with bromine was approx. tenfold higher compared to the chlorine treatment. The higher amounts can be only partially explained by the twofold bromine concentrations applied and by the higher molecular weight of bromine compared to chlorine, resulting in higher µg/L concentrations. In direct comparison, bromine as a.s. generated higher amounts of DPBs analysed in the present study. At different chlorine concentrations the amount of DBPs was increasing with increasing a.s. concentration, while different bromine concentrations deliver a less obvious result. The high amounts of HAAs determined at low bromine concentration of 20 µg/L resulted in total DBP amount higher than determined at bromine concentration of 100 µg/L. Mainly responsible for this result was the decreasing concentration of TBAA. As TBAA is unstable, the lower concentration at 100 µg/L compared to 20 µg/L could be at least partially caused by decomposition of TBAA. For both a.s., the majority of the DBPs produced was assigned to the DBP classes trihalomethanes (THMs) and haloacetic acids (HAAs). The groups of THMs and HAAs accounted for almost all DBPs generated using bromine as a.s. and more than half of the DBPs formed using chlorine as a.s.. Figure 6 clearly

shows the higher number of different DBP classes generated after treatment with chlorine compared to bromine. Further important DBP classes detected after treatment with chlorine were HALs and HANs. A possible reason for the high occurrence of THMs and HAAs was that these two DPB classes and especially THMs, represent final reaction products of the matrix with the two a.s.. Higher molecular weight halogenated DBPs formed originally, may have decomposed into lower molecular weight DBPs. Through hydrolysis or decarboxylation reactions, the groups of haloacetonitriles (HAN), haloacetic acids (HAA), haloketones (HK), haloacetamides (HAM) can decompose into trihalomethanes. (El-Athman et al., 2021).

Figure 6: Sum concentration of DBP classes generated using different hypochlorite (left) or hypobromite (right) concentrations

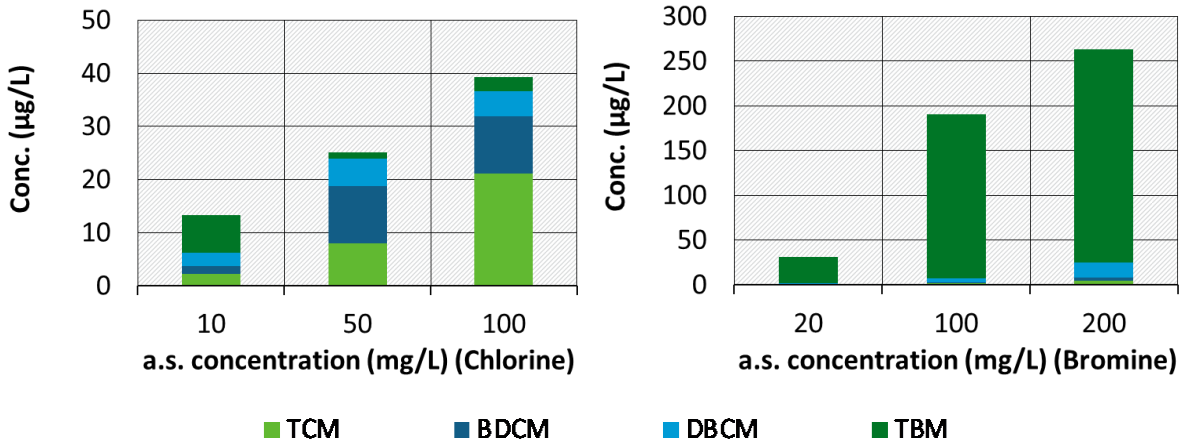


Source: own illustration, diagrams with experimental results

A detailed view on the THMs (Figure 7) and HAAs (Figure 8) shows the dominating representatives within these DBP classes. For bromine, for THMs it was tribromomethane (TBM) and di- (DBAA) and tribromoacetic (TBAA) acids were the dominating HAAs. Chlorinated THMs and HAAs were almost negligible. The result was more differentiated when chlorine was applied as a.s.. As expected, chlorinated THMs and HAAs were the main part of the found DBPs within these DBP classes, but also brominated and iodinated DBPs were present at significant amounts. The reason for formation of brominated or iodinated DBPs was the bromide and iodide content in the swimming pool matrix. As the amounts of the added bromide (500 µg/L) and iodide (25 µg/L) were low compared to the chlorine concentrations, the reactive species in the experiments mainly consisted of hypochlorous acid/hypochlorite (HOCl/OCl-). This explains the formation of preferential chlorinated DBPs. Regarding the amounts of single DBPs within the group of THMs after use of chlorine, an increase in chloroform (TCM) and bromodichloromethane (BDCM) could be seen with increasing chlorine concentrations. At the same time, a decrease in dibromochloromethane (DBCM) and tribromomethane (TBM) was observed. One reason for this development was the changing ratio of iodide and bromide compared to the chlorine. Generally, a part of the added bromide is oxidised to free bromine (HOBr/OBr-). Free bromine reacts as a.s. faster with the existing matrix than hypochlorite, leading to a comparably high proportion of formed TBM at lowest free chlorine concentration (10 mg/L) (Westerhoff et al., 2004). With increasing a.s. concentration, the excess of hypochlorite was dominating the reaction with the matrix leading to lower amount of TBM formed. However, this effect was not supported by the amounts of HAAs observed at different chlorine concentrations. Within the HAAs increasing chlorine concentration led to the

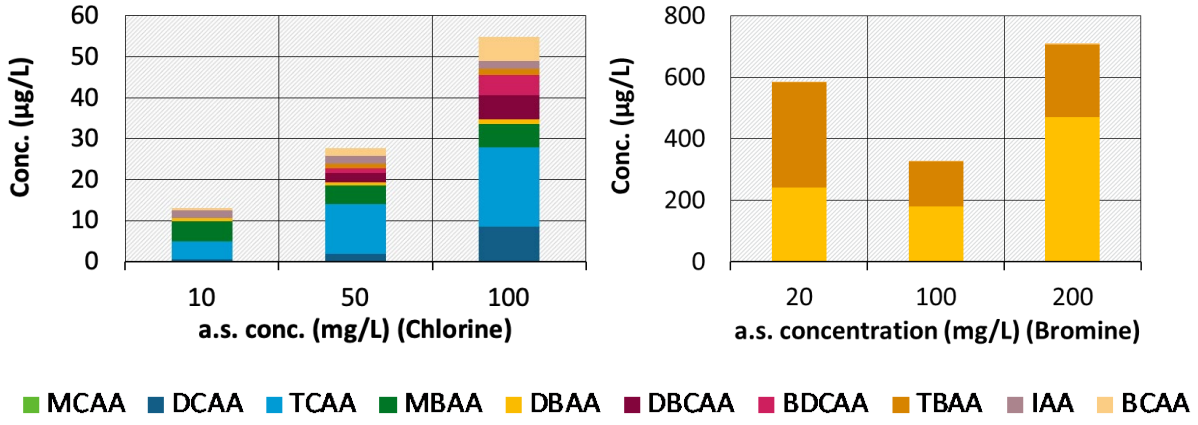
generation of more higher substituted (di- or three halogenated) HAAs, both chlorinated and brominated, while the amount of monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA) was constant or slightly decreasing. Compared to chlorine, which has a stronger oxidising effect, bromine could also act preferentially as a substitution halogen (Westerhoff et al., 2004).

Figure 7: Trihalomethanes (THMs) generated at different hypochlorite (left) or hypobromite (right) concentrations



Source: own illustration, diagrams with experimental results

Figure 8: Haloacetic acids (HAAs) generated at different hypochlorite (left) or hypobromite (right) concentrations (possible decomposition of TBAA in sample applied with 100 mg/L bromine)

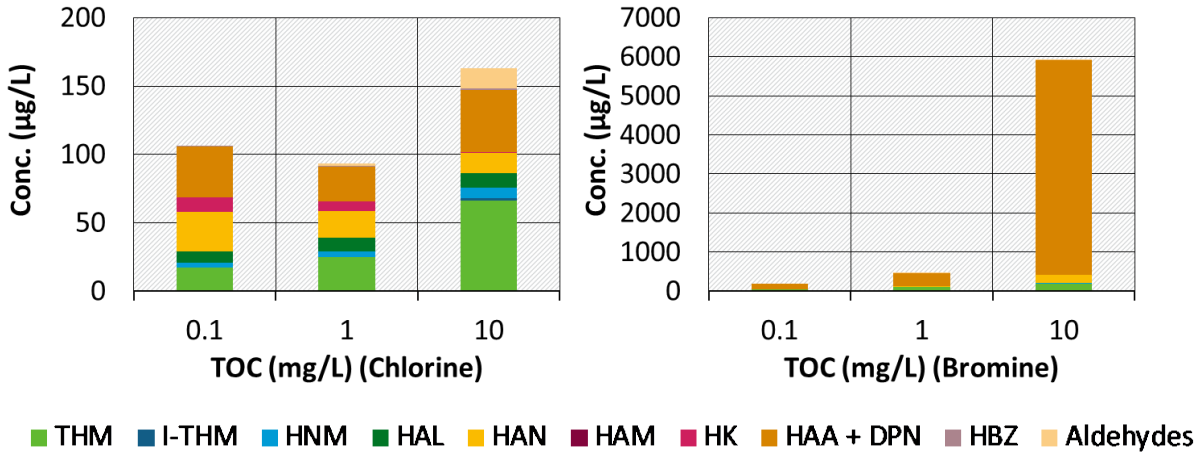


Source: own illustration, diagrams with experimental results

Variation of total organic carbon (TOC) concentrations

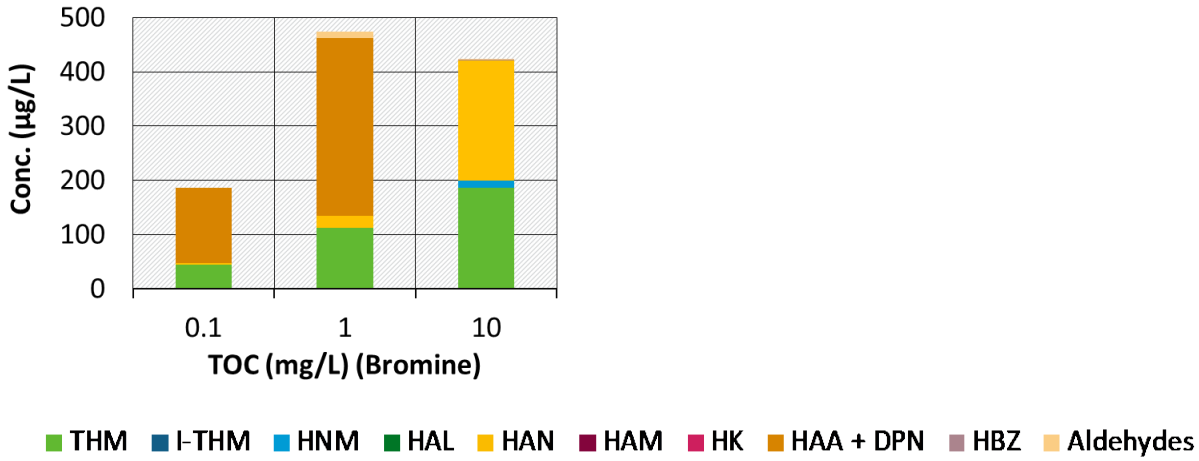
The influence of the TOC concentration was investigated using 3 different load concentrations. In swimming pools, TOC concentration is a representative of the load from bathers, which is the main source of pollution. Figure 9 shows the total amount of DBPs generated. The concentration determined for HAAs at highest TOC load (10 mg/L) after treatment with bromine was exceptionally high. Although it is theoretically possible that approx. 6 mg/L HAAs were generated in a solution with 10 mg/L TOC and 100 mg/L bromine, but in this case a main part of the TOC would have been quite selectively transformed into the two HAAs DBAA and TBAA. This seems very unlikely, especially considering the results of the other simulations with bromine. Therefore, either analytical problems or an experimental error was assumed to be the reason for this result. No other convincing explanation was found and therefore this single result was not further discussed. The data was presented additionally without the questionable value in Figure 10. As observed for the variation of a.s. concentration, the DBP amount after treatment with bromine was significantly higher compared to the chlorine treatment, while the treatment with chlorine led to generation of more different DBPs. With increasing TOC concentration, the absolute amount of DBPs produced also increased in the most cases. Karanfill et al. were also able to show that increasing TOC concentrations were accompanied by increased DBP formation (Kanan et al., 2015). However, the general trend was not observed for the lowest TOC loading (0.1 mg/L) and treatment with chlorine. In this case the total concentration of DBPs was slightly higher than determined for the middle TOC loading (1 mg/L). Among the DBP classes THMs and HAAs are found at highest concentrations for both a.s.. Other DBP classes detected at significant concentrations using chlorine as a.s. were HANs, HALs and HKs. The concentration of HALs was not changing for the different TOC concentrations, while the concentrations of HANs and HKs were interestingly decreasing. This indicates that the generation of particular DBPs may depend on the ratio of TOC and the a.s. used, i.e. changing TOC concentrations influenced not only the amount but also the composition of the generated DBPs. A significant number of aldehydes was only observed for the highest TOC concentration. After treatment with bromine, additionally to THMs and HAAs, HANs were observed at significant concentrations, which were increasing with the TOC loading. Furthermore, HNMs were observed at elevated amounts for highest TOC loading.

Figure 9: Sum concentration of DBP classes generated using different TOC concentrations for hypochlorite (left) and hypobromite (right) as a.s. (questionable HAA result at 10 mg/L TOC and bromine treatment)



Source: own illustration, diagrams with experimental results

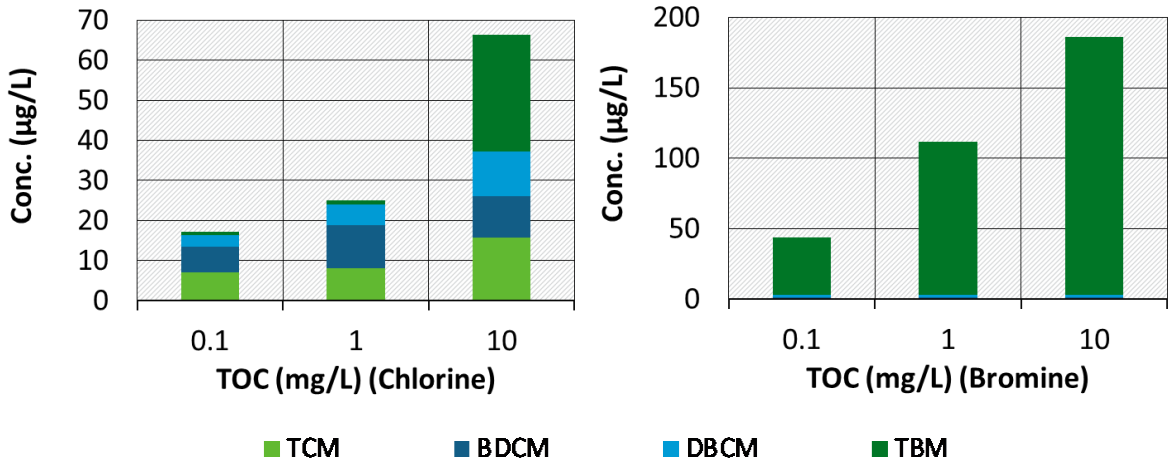
Figure 10: Sum concentration of DBP classes generated using different TOC concentrations for hypobromite as a.s. without questionable HAA result at 10 mg/L TOC concentration



Source: own illustration, diagram with experimental results

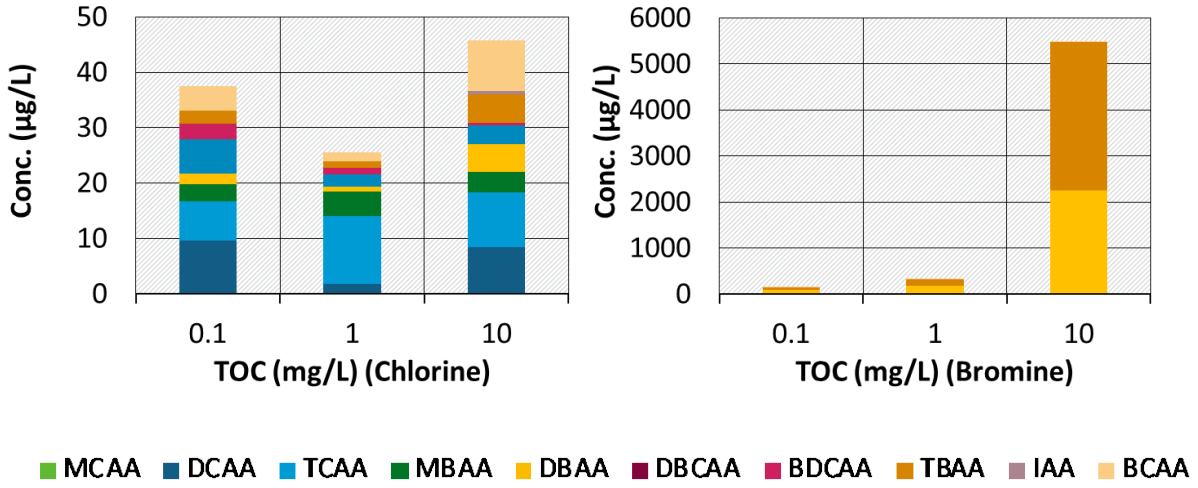
Regarding single DBPs of THMs and HAAs, as shown in Figure 11, Figure 12 and Figure 13, similar observation as for the a.s. concentration variation were made also for the variations of TOC loading in experiments with bromine as a.s.. TBM dominated the group of THMs, the other THMs were observed at concentrations lower by two orders of magnitude and the same was true for DBAA and TBAA regarding the HAAs. Generally, almost no chlorinated DBPs were detected after treatment with bromine. In contrast, in the chlorine tests all THMs and HAAs were detected. Among the THMs, TCM and DBCM concentration increased steadily, whereas no systematic progress is observed for BDCM showing similar values for all TOC loadings. For TBM, an abrupt increase in the highest TOC loading (10 mg/L) could be seen. As the total amount of HAA was lowest for the middle TOC loading systematic interpretation was complicated. Especially at the middle TOC loading a comparably low concentration of DCAA and a high concentration of TCAA were observed. Similar differences with respect to the chlorination degree were also observed for the control experiments, but no explanation could be given for the observation. Except this result, highest concentrations were observed for TCAA and DCAA. DBCAA was observed at higher concentrations at low TOC loading, while DBAA, TBAA and BCAA were observed at higher concentrations at low TOC loading. The results, especially regarding the concentration of single DBP at different TOC loadings, indicated the complex chemical reaction conditions and interaction in the simulation mixture. The exact processes for these observations cannot be explained and therefore clear conclusions regarding potential worst-case scenarios cannot be made easily. Nevertheless, regarding both, THMs and HAAs after application with chlorine, generally an increasing amount of brominated DBPs was observed with increasing TOC loading. As with increasing TOC loading the ratio of bromide to chlorine in the simulation mixtures was increasing, the observation confirmed the results of the previous experiments with respect to the fast reaction of bromine generated from bromide, if present at a sufficient ratio.

Figure 11: Trihalomethanes (THMs) generated using different TOC concentrations for hypochlorite (left) or hypobromite (right) as a.s.



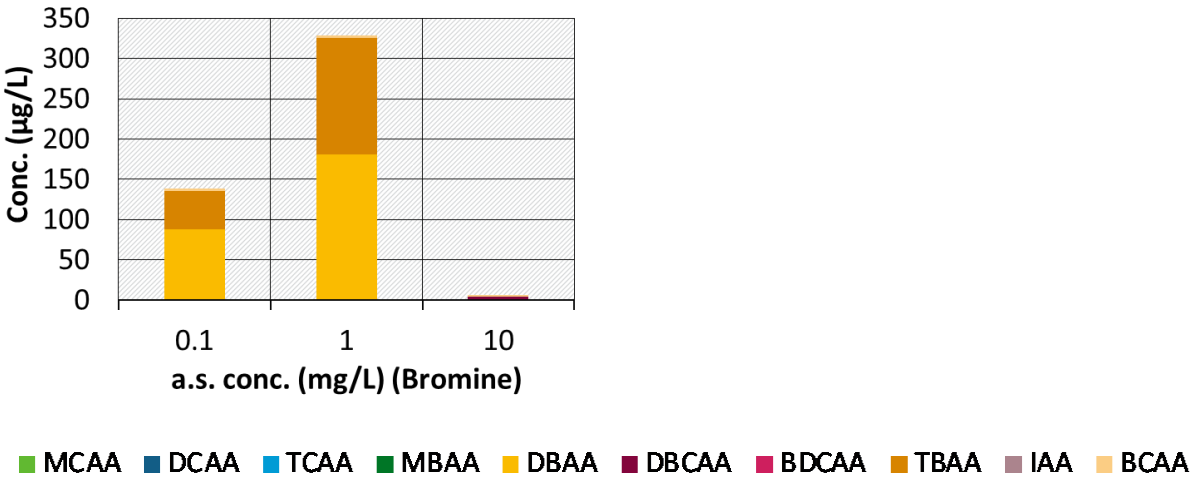
Source: own illustration, diagrams with experimental results

Figure 12: Haloacetic acids (HAAs) generated using different TOC concentrations for hypochlorite (left) or hypobromite (right) as a.s (questionable DBAA and TBAA result at 10 mg/L TOC concentration)



Source: own illustration, diagrams with experimental results

Figure 13: Haloacetic acids (HAAs) generated using different TOC concentrations for hypobromite as a.s without questionable DBAA and TBAA result at 10 mg/L TOC concentration

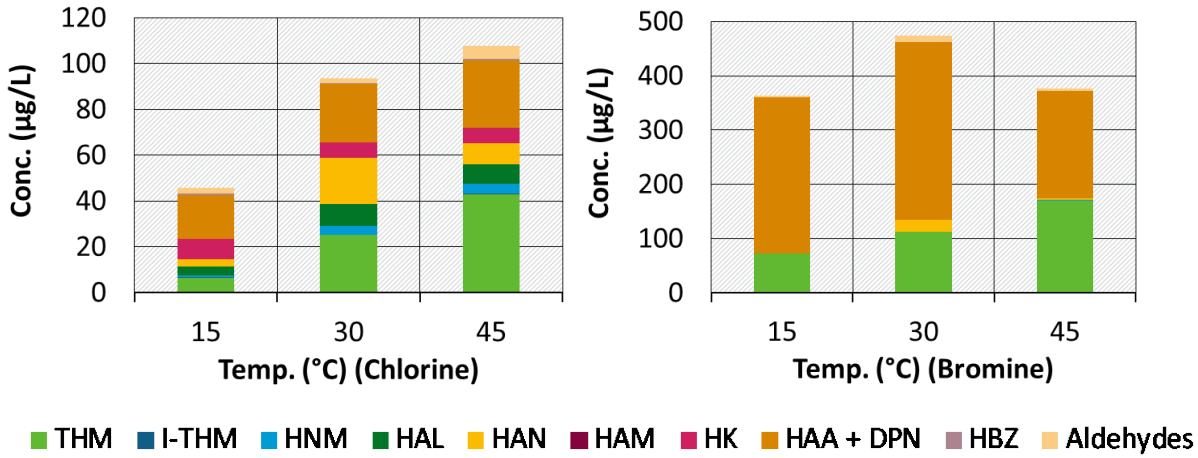


Source: own illustration, diagram with experimental results

Variation of reaction temperature

The simulations of disinfection processes with the swimming pool matrix were performed at three different temperatures. The influence of the temperature on the total amount of generated DBPs is shown in Figure 14. Comparison of overall results with chlorine and bromine as a.s. confirmed the previous findings. The total DBP amount after treatment with bromine was approx. five- to tenfold higher compared to the chlorine treatment and only two different DBP classes, THMs and HAAs, were detected after the bromine treatment, while after chlorine treatment DBP from more different classes are detected. In simulations with chlorine, increase of reaction temperature led to the expected increase of the total amount of generated DBPs. However, the total increase of DBPs was significantly higher from 15°C to 30°C as from 30°C to 45°C. Regarding the single DBP classes, the temperature dependency was more complex. The amounts of THMs and HAAs, the both DBP classes observed at highest amounts, was continuously increasing with the temperature, but the amount of HAN decreased form 30°C to 45°C, while the amount of HALs was quite constant for all three temperatures and the number of HKs at least for 30°C and 45°C. No systematic influence of the temperature on the total DBP amounts was observed in simulations applied with bromine. The amounts increased from 15°C to 30°C and decreased again from 30°C to 45°C. As observed for the other parameter variations, THMs and HAAs were dominating the formed DPBs and additionally noticeable amounts of HANs and aldehydes were only generated at 30°C. The amount of THMs showed the expected increase with reaction temperature, while the amount of HAAs significantly decreased from 30°C to 45°C. The partially unexpected influence of the temperature on DBP formation again showed the complexity of the reaction mixtures in the disinfection simulations. The observed decease of DBP amounts with increasing temperature may have several reasons. As mentioned before, some DBPs react further to form other DBPs (El-Athman et al., 2021), which could be accelerated by increasing temperature. Furthermore, increasing temperature would accelerate the different reactions not by the same factor, which may lead to change of the ratio of formed DBPs at different reaction temperatures. In both cases, this would lead to increasing total amounts of DBPs, however if the formed DBPs were out of the analytical scope of the present study, this would not be observed.

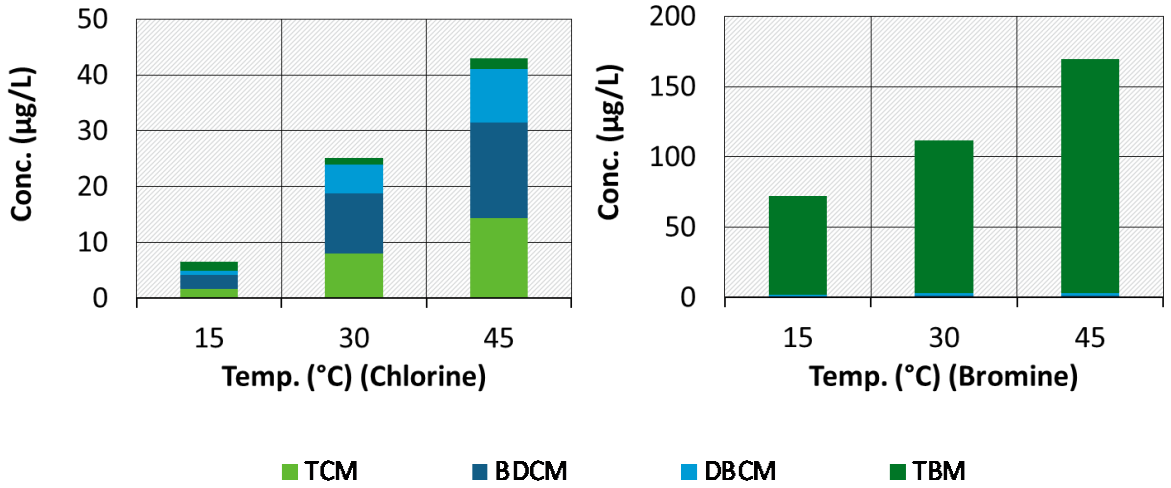
Figure 14: Sum concentration of DBP classes generated at different reaction temperatures for hypochlorite (left) and hypobromite (right) as a.s.



Source: own illustration, diagrams with experimental results

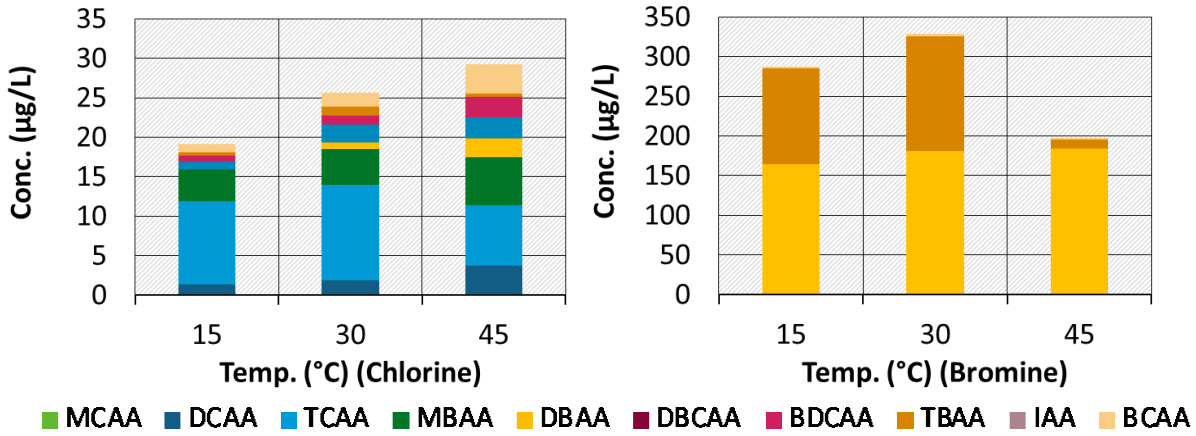
For all single THMs, increase of the reaction temperature led to an increase in the generated amounts for both investigated a.s., as shown in Figure 15. After treatment with chlorine all four THMs were observed, with TBM at significantly lower amounts compared to the other three THMs. As observed earlier, treatment with bromine resulted in the generation of TBM. The reason for the expected and quite clear influence of the temperature on the amounts of formed THMs could be, that THMs are a final reaction product within the halogenated DBPs. As THMs will not react any further, the dependency on temperature was less complex. The most different representatives of HAAs were detected using chlorine as a.s., with TCAA observed at highest amounts for at all three temperatures but at a significantly deceasing amount from 30°C to 45°C (Figure 16). The amounts of DCAA, MBAA, DBCAA and BDCAA and BCAA continuously increased with increasing temperature. Generally, increasing temperature led to an increasing ratio of brominated HAAs. Again, only the brominated HAAs, DBAA and TBAA were detected after treatment with bromine. The decrease of both trihalogenated HAAs, TCAA and TBAA from 30°C to 45°C was remarkable. However, as both are further hydrolysed to the corresponding THMs (El-Athman et al., 2021) and especially TBAA is unstable, this decrease with increasing temperature may be caused by accelerated hydrolysis or other reaction of TCAA and TBAA.

Figure 15: Trihalomethanes (THMs) generated at different reaction temperatures for hypochlorite (left) or hypobromite (right) as a.s.



Source: own illustration, diagrams with experimental results

Figure 16: Haloacetic acids (HAAs) generated at different reaction temperatures for hypochlorite (left) or hypobromite (right) as a.s.



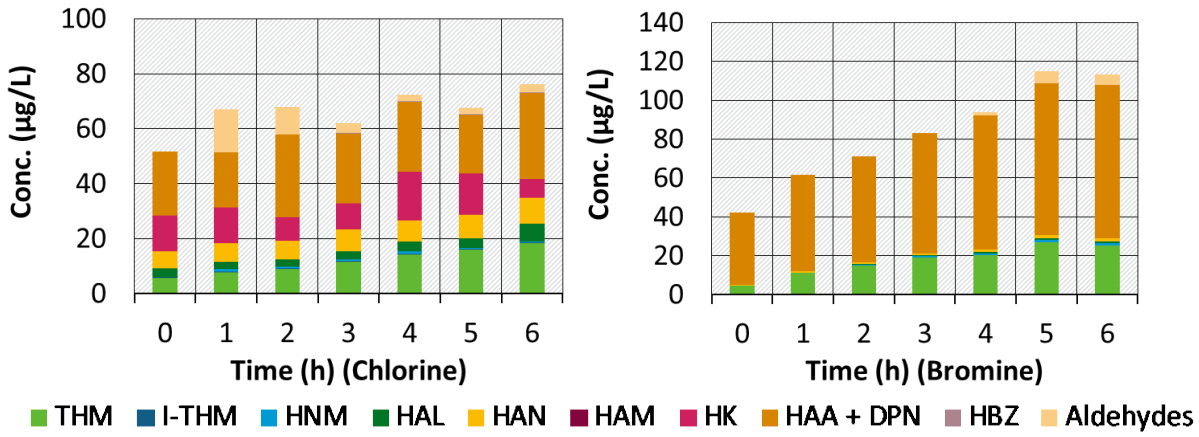
Source: own illustration, diagrams with experimental results

Variation of time (kinetic experiment)

The kinetics of the DBP formation were investigated using 7 individual samples for up to 6h reaction time. Figure 17 shows the total amount of detected DBPs of the different DBP classes. In the experiments applied with chlorine, a time dependency of the total DBP amount was only visible for the first two measurement points. Afterwards, the total amount of DBP was at about 70 µg/L and was not changing continuously with time. Furthermore, a total DBP concentration of 50 µg/L was observed already in the start sampling (0h). Considering that in the corresponding simulation (same parameter setup, see Figure 14, 30°C values) approx. 90 µg/L were determined after 24h, it is obvious that DBP formation occurs fast and could not be resolved in the performed experiment. Nevertheless, some indications were possible from the values of the single DBP classes. THMs were the only DPB class where a continuous increase over the observation time of 6h was determined. The reason may be again, that THMs are a final product of the DBP formation. The highest concentrations were determined for HAAs, within the rage of 20 µg/L – 30 µg/L for all sampling time points. Also, concentrations of HANs and HALs

were quite constant over time, indicating that either the concentrations were static or the formation and degradation were occurring at comparable rates. Aldehydes were observed at highest concentration after 1h and afterwards the concentration was decreasing, which indicates a degradation to other DBP. No continuous time dependence was observed for HKs, however their concentration showed quite a variation between 7 µg/L and 18 µg/L over time indicating the complex processes in the simulation mixture. Although also for bromine as a.s. a comparable DBP concentration was observed at the start sampling (0h) as for chlorine, a continuous increase to concentrations of approx. 110 µg/L was observed. This is understandable regarding the total DBP concentration in the corresponding simulation (same parameter setup, see Figure 14, 30°C values) after 24h of approx. 450 µg/L and the value of 110 µg/L after 6h correlates quite well with the value of 450 µg/L after 24h. Again, only the DBP classes of THMs and HAAs were detected at significant amounts and both were continuously increasing with time.

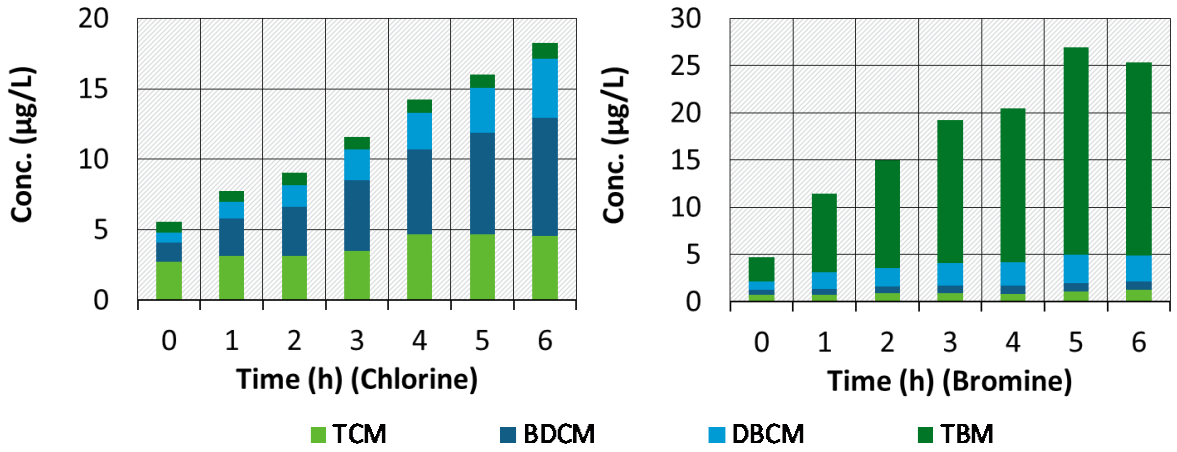
Figure 17: Sum concentration of DBP classes generated after different reaction times for hypochlorite (left) and hypobromite (right) as a.s.



Source: own illustration, diagrams with experimental results

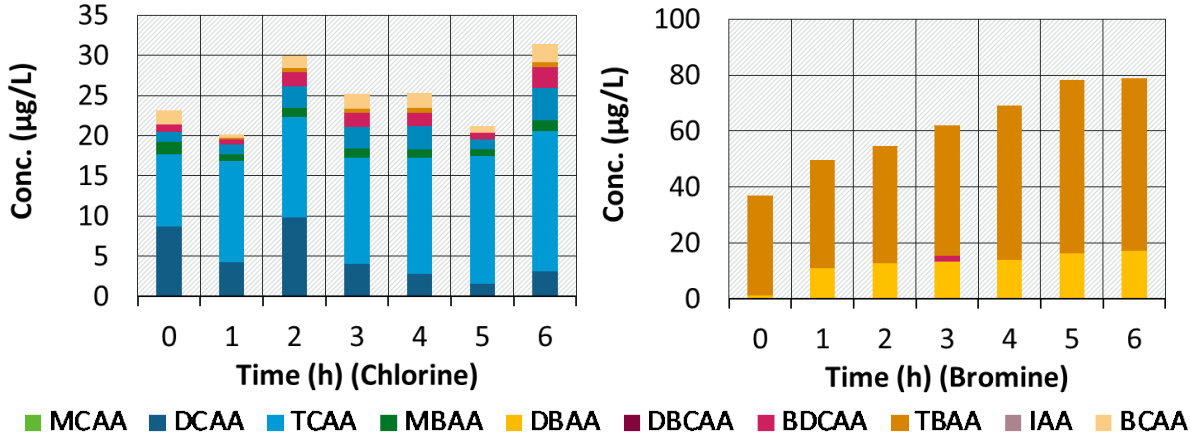
The concentrations values for single THMs and HAAs are presented in Figure 18 and Figure 19. Interestingly, after treatment with chlorine, the concentration of TCM was high in relation to the other THMs but with time, the ratio of TCM was continuously decreasing, while the ratios especially of BDCM and DBCM are continuously increasing. In a general view, the degree of bromination within the THMs was increasing with time. Among the single HAAs in the kinetic experiment with chlorine only rough tendencies could be derived. Within the observation time the amount of DCAA was decreasing, while the amount of TCAA was increasing. The increase of the chlorination degree with time was expectable. Furthermore, as observed for the THMs, the amount of the brominated HAAs, DBCAA, BDCAA and BCAA was increasing with time. After application of bromine, TBM was the most dominant THM and was continuously increasing with reaction time. In case of the HAAs the same was true for TBAA. In contrast to most previous observation, DBAA was observed at lower ratios compared to TBAA. A reason could be, that at the beginning of the reaction time the formation of TBAA was faster compared to the degradation, which changed in the course of the reaction, resulting in a changing ratio of TBAA and DBAA.

Figure 18: Trihalomethanes (THMs) generated after different reaction times for hypochlorite (left) or hypobromite (right) as a.s.



Source: own illustration, diagrams with experimental results

Figure 19: Haloacetic acids (HAAs) generated after different reaction times for hypochlorite (left) or hypobromite (right) as a.s.



Source: own illustration, diagrams with experimental results

6.6.3 Laboratory simulations with general matrix in solution

After treatment of the general matrix with chlorine, higher concentrations of DBPs were detected compared to the values observed for the swimming pool matrix. The analytical results are summarised in Table 45, Table 46, Table 47 and Table 48 for the kinetic experiments. Although again DPBs from most of the analysed DBP classes were found, only few single DBPs were dominating the total DBP amount. Similar to experiments with the swimming pool matrix, HAAs were found at high concentrations, but the concentrations of THMs were less dominant and detected at same ranges as HALs. The highest amounts of HAAs were 742.3 µg/L observed in the experiment with elevated temperature (45°C). However, this result was influenced by the unexpectedly low amount of HAAs at highest TOC concentration (100 mg/L). Although the LC-MS/MS analysis was problematic in presence of the general matrix and the results need to be regarded carefully, this observation is discussed in more detail below. Among the HAAs, only the chlorinated ones were detected, dominated by DCAA and TCAA. TCM was by far the THM found at highest concentrations, with a maximum of 105.7 µg/L at highest TOC concentration. This was

also true for trichloroacetaldehyde (TCAL) within the HALs, with 357.3 µg/L detected in the simulation at highest TOC concentration. Acetaldehyde was by far the dominant aldehyde and maximal amounts of 947.5 µg/L were found at highest TOC concentration. This unexpectedly high concentration is also discussed in more detail below. Among all DBP classes, iodinated DBPs were not detected at all and brominated only at low concentrations. This could be expected, as the general matrix was not spiked with bromide and iodide and the natural occurrence of these anions in the general matrix is low.

Completely different results were obtained using hydrogen peroxide in disinfection simulations with general matrix, summarised in Table 49, Table 50 and Table 51 for the kinetic experiment. Although in some literature formation of halogenated DBPs after the use of peroxides was reported (Zhang et al., 2013; Shah et al., 2015; Dell'Erba et al., 2007; Chu et al., 2016), no halogenated DBPs were determined in the simulation experiments performed within the present study. As most of the analysed DBPs within the analytical scope were halogenated DBPs, only few DBP from the class of aldehydes were identified at all. Also, the detected concentrations were low compared to the experiments described before. Acetaldehyde was detected at a maximal concentration of 22.3 µg/L in the simulations at highest TOC concentration (100 mg/L). Further detected DBPs were acetophenon, benzaldehyde, propanal and nonenal, but their concentration never exceeded 4 µg/L. The reactivity of hydrogen peroxide is differing from chlorine and bromine, as only the reactivity as oxidation agent is present but no halogenation takes place. Nevertheless, hydrogen peroxide is a reactive oxidation agent capable of unselective reactions with organic compounds and thus the generation of DBPs. Hydrogen peroxide may be less reactive compared to chlorine or bromine, but it is assumed that the experimental results of the present study underestimate the DBP formation potential of hydrogen peroxide and peroxides in general. An important result of the literature search on DBPs (see chapter 2.3.5) is the strong bias on chlorinating a.s. for disinfection uses. As a consequence the analysed DBPs were mostly correlated to the use of chlorinating a.s.. This was considered for the choice of analytes by including several non-halogenated DBPs as these were expected to dominate the DBPs generated by peroxides. As the chosen potential DBPs were detected only at comparably low concentrations, it is assumed that DBPs relevant for the use of peroxides were out of the analytical scope of the present study.

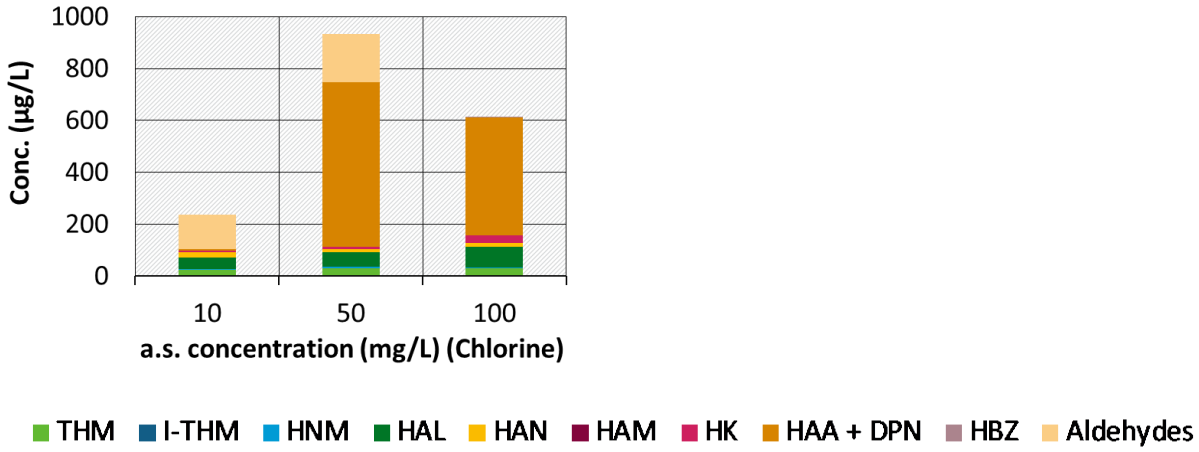
Variation of the chlorine and hydrogen peroxide concentrations

The influence of chlorine and hydrogen peroxide concentration was investigated using three different a.s. concentrations. The amount of DBPs found after treatment of the general matrix with hydrogen peroxide was very low compared to the results in the simulations with general matrix and chlorine. As described in previous chapter, the general DBP formation potential of hydrogen peroxide is estimated to be higher as observed in the present study and it is assumed that major DBPs relevant for the use of hydrogen peroxide were not included in the list of analysed substances. For this reason, no figures for hydrogen peroxide are shown. For the DBPs detected in simulations with hydrogen peroxide, no influence of the a.s. concentration on DBP formation was observed. The simulations with variation of hydrogen peroxide concentration were not analysed by GC-MS because in experiments with variation of TOC concentrations (see below) none of the respective DBPs were found.

Figure 20 shows the total amount of DBPs generated after treatment of general matrix with chlorine as a.s.. Similar to the simulations with chlorine and the swimming pool matrix, treatment of general matrix with chlorine led to formation of DBPs from the most DBP classes and the total determined DBP concentrations were even higher. The influence of the a.s. concentration is quite different among the DBP classes and not easy to interpret. HAAs were observed at an explicitly low concentration for the low chlorine concentration and the amount

increased by approx. two order of magnitude for the middle chlorine concentration and decreased again in the simulation with high chlorine concentration. The later observation was also true for the aldehydes and in both cases quite unexpected. The reason for the unexpectedly low HAA concentration in the disinfection simulation at low chlorine concentration may be alternative reactions of the chlorine in excess of the matrix, e.g. oxidation reactions leading to formation of aldehydes found at quite high amounts at low chlorine concentration. At higher chlorine concentration, the higher ratio of the a.s. in relation to the matrix led to further reactions and the formation of DBPs resulting from multiple reactions like HAAs (see Figure 24). Amounts of HALs and HKs were both continuously increasing with increasing chlorine concentrations. While HALs were found at significant concentrations at all a.s. levels, a significant formation of HKs is only observed at the highest chlorine concentration. Compared to the simulations with swimming pool matrix, THMs were a less dominant class of DBPs in presence of the general matrix and their amount was not significantly changing for the different chlorine concentrations. HANs were the last DBP class found at significant concentrations and the highest amounts were found for the lowest chlorine concentrations and in the same range for the middle and the high chlorine concentrations. Overall the results of the simulations at different chlorine concentrations showed, similar to the swimming pool matrix, complex reaction conditions. Consequently, not all observations could be clearly explained, especially because possible analytical issues additionally complicate the evaluation.

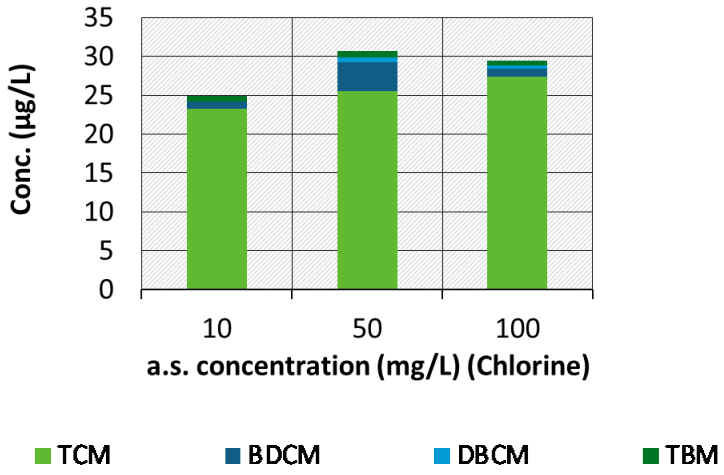
Figure 20: Sum concentration of DBP classes generated using different hypochlorite concentrations



Source: own illustration, diagram with experimental results

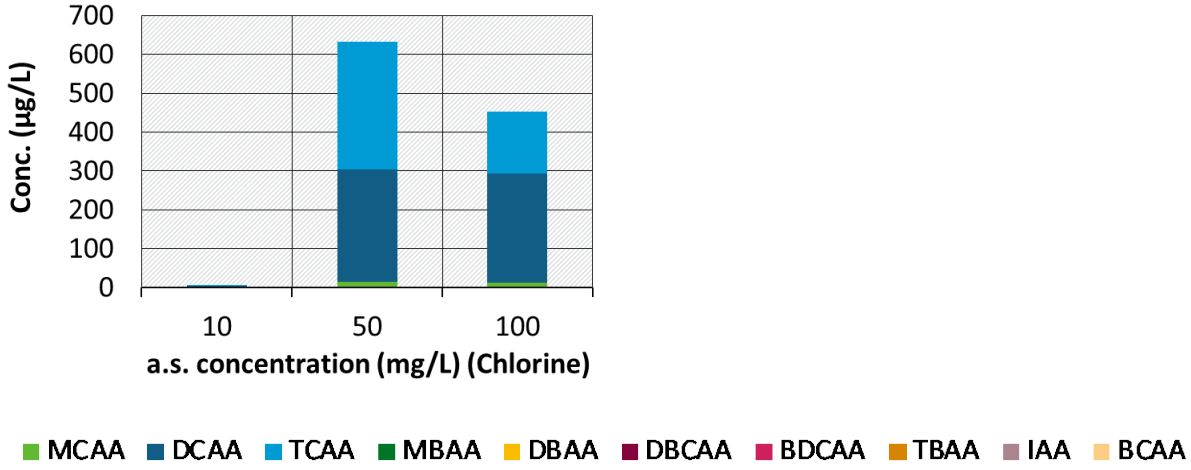
Regarding single DPBs from the classes of THMs (Figure 21) and HAAs (Figure 22), it is obvious that both DBP classes were dominated only by few particular substances. For the THMs it was TCM, while for the HAAs DCAA and TCAA were by far the main detected DBP. Only very low concentrations of brominated THMs and no brominated HAAs were found. The amounts of the single THMs showed no clear dependence on a.s. concentration and the results for HAAs were reflecting a complex and thus not easy to interpret dependence on the a.s. concentration, indicating that the changing ratio of matrix to a.s. led to changing DBPs ratios in the simulation experiments. At the same time some influence of the matrix on the analytical results additionally complicating the interpretation cannot be excluded.

Figure 21: Trihalomethanes (THMs) generated at different hypochlorite concentrations



Source: own illustration, diagram with experimental results

Figure 22: Haloacetic acids (HAAs) generated at different hypochlorite concentrations



Source: own illustration, diagram with experimental results

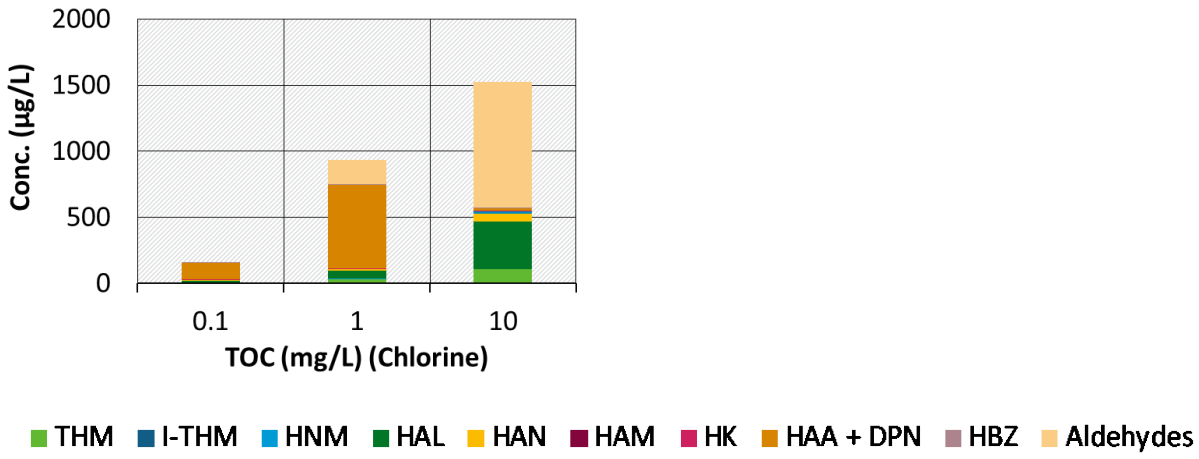
Variation of total organic carbon (TOC) concentrations

The TOC concentration of the general matrix was varied in the same range as for the swimming pool matrix, applying concentrations of 0.1 mg/L, 1 mg/L and 10 mg/L. The total amounts of detected DBPs are summarized as DBP classes in Figure 23. Values obtained using hydrogen peroxide as a.s. were not presented in the figure, because the detected concentrations were low (see Table 49 and Table 50), confirming the results obtained in the simulations using different a.s. concentrations. The only DBPs detected were three aldehydes. Acetaldehyde with a maximal concentration of 22.3 µg/L in the simulation with the highest TOC concentration and furthermore propanal and benzaldehyde with maximal concentration of 2.5 µg/L and 0.4 µg/L, respectively. Analysis of GC-MS analytes was only performed for the TOC variations. As none of the included substances was detected at all, the other parameter variations with hydrogen peroxide as a.s. were only analysed by LC-MS/MS.

Application of chlorine as a.s. led, as observed for the variation of a.s. concentration, to formation of DBPs from the most DBP classes. The interpretation of the results for the TOC variations was not as easy as for the variation of the a.s. concentrations. The pronounced decrease of HAA concentration between the 1 mg/L and 10 mg/L TOC concentration was unexpected. However, considering the results of the a.s.

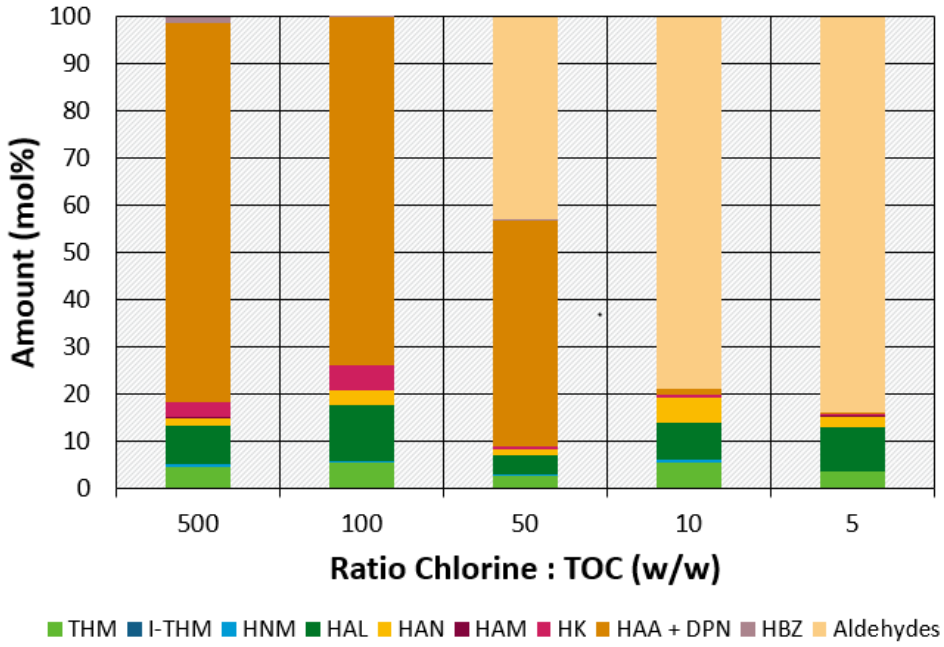
variation, in detail for 10 mg/L and 50 mg/L chlorine concentrations, similar observations were made. At high TOC to chlorine ratios (10 mg/L chlorine in simulation with a.s. variation and 10 mg/L TOC in in simulation with TOC variation) unexpectedly low concentrations of HAAs were detected and at the same time high concentrations of aldehydes. The rates of HAAs and aldehydes changed with decreasing TOC to chlorine ratios (50 mg/L chlorine in simulation with a.s. variation and 1 mg/L TOC in in simulation with TOC variation). The influence of the chlorine:TOC ratio is presented in Figure 24.

Figure 23: Sum concentration of DBP classes generated using different TOC concentrations with hypochlorite



Source: own illustration, diagram with experimental results

Figure 24: Sum concentration of DBP classes (as mol%) generated at different chlorine:TOC ratios



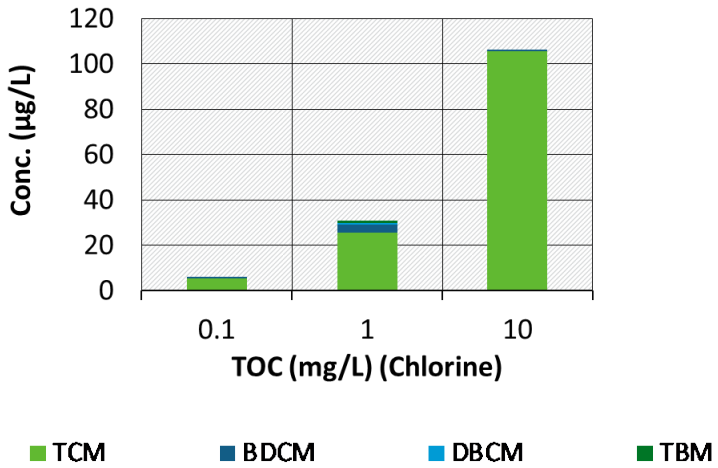
Source: own illustration, diagram with experimental results

For the figure data of the simulations with a.s. and TOC concentration variation was evaluated. The simulations were sorted according to the chlorine:TOC ratio, resulting in five data sets. The DBP concentrations were converted from weight to molar concentrations in a first step and finally displayed as mol% for each of the shown DBP classes. Regarding HAAs and aldehydes, the evaluation confirms that at excess TOC primary aldehydes (mostly acetaldehyde) were

generated and with rising chlorine rates these aldehydes further react and HAAs are increasingly generated. This is also true for HAM and HBZ only observed at high chlorine rates. However, amounts of other halogenated DBP classes like THMs, HALs and HANs show no systematic dependence on the chlorine:TOC ratio, therefore the evaluation delivers only a partial explanation of the results. As the exact reaction routes of the DBP formation are unknown, it is not possible to bring all data in a reasonable dependence to each other. The analysis by GC-MS and the LC-MS/MS data for the low and middle TOC concentration showed further results. A very significant increase of total DBP amount was observed with increasing TOC concentrations and the total amount of DBP at high TOC concentration was higher compared to high a.s. concentration. Similar observation was made for the swimming pool matrix, but the data for the general matrix was much more significant. It seems, that, at least within the parameter matrix of the performed simulations, the TOC availability has a bigger influence on DBP formation compared to a.s. availability. Among the single DBP classes, highest amounts were detected for HAAs and the amount increases significantly from low to middle TOC concentration. HALs were also observed at high concentrations. Their amount is increasing continuously with increasing TOC concentration with an extraordinary increase from approx. 60 µg/L (TOC: 1 mg/L) to approx. 360 µg/L (TOC: 10 mg/L). Treatment of general matrix with chlorine led obviously to generation of significantly more HALs and non-halogenated aldehydes compared to the swimming pool matrix. Further DBP classes continuously increasing with increasing TOC concentration and detected at significant amounts were THMs and HANs. Similar to HALs, for both a remarkable increase is observed from the middle to the high TOC concentration.

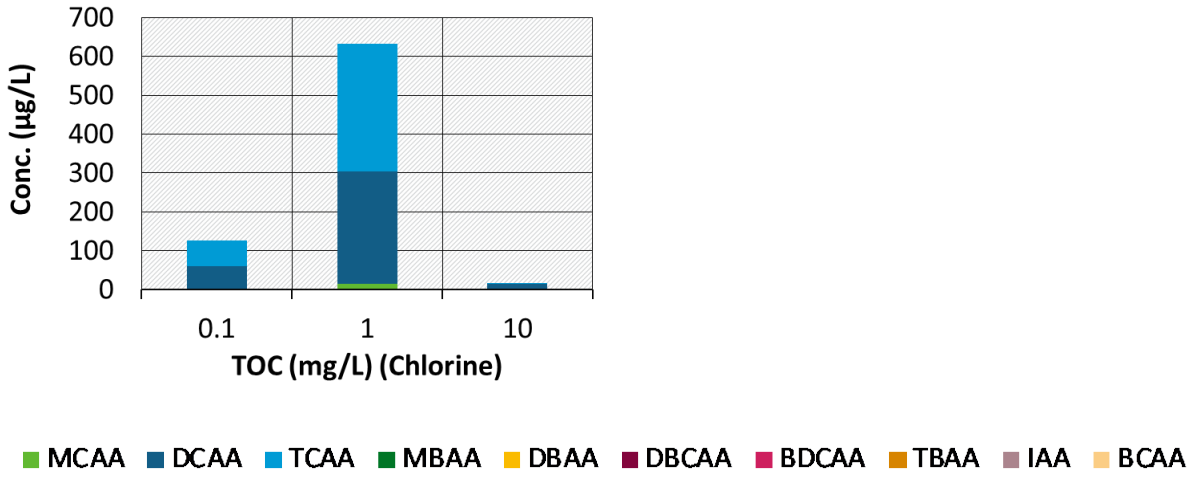
As illustrated by Figure 25 and Figure 26 the DPB classes of THMs and HAAs were, as already observed in simulations with variation of the a.s. concentration, dominated by three substances. TCM was the dominant THM and TCAA and DCAA were the most important HAAs. Similar observation was also made for the other DBP classes observed (see Table 45 and Table 46). Among non-halogenated aldehydes, acetaldehyde was observed by far at highest concentration and for HALs it is the structurally related trichloroacetaldehyde. Finally, the dominating HAN was dichloroacetonitrile. Similar as in simulations with variation of the a.s. concentration, brominated DBP were detected only occasionally and at low concentrations.

Figure 25: Trihalomethanes (THMs) generated using different TOC concentrations for hypochlorite as a.s.



Source: own illustration, diagram with experimental results

Figure 26: Haloacetic acids (HAAs) generated using different TOC concentrations for hypochlorite as a.s.



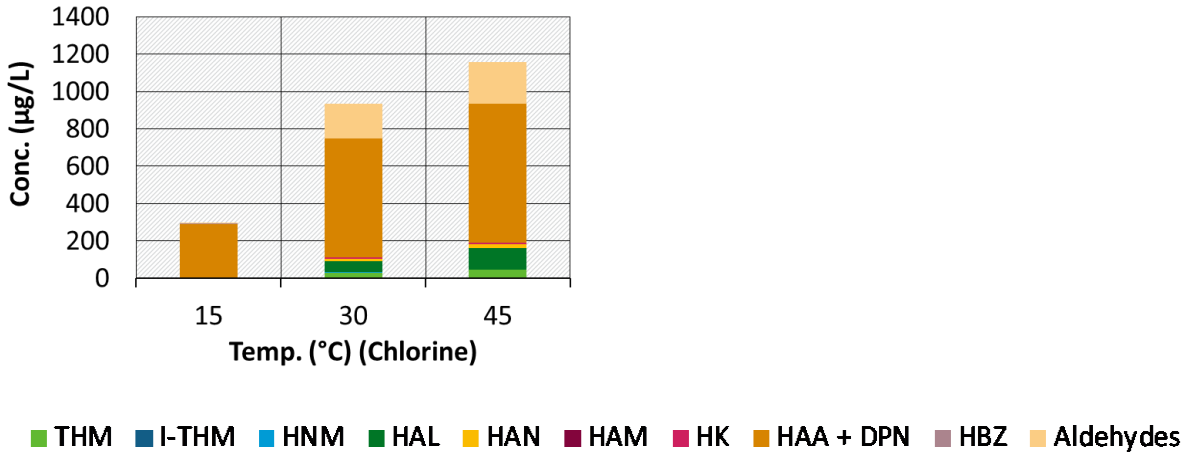
Source: own illustration, diagram with experimental results

Variation of reaction temperature

The dependency of DBP formation on the temperature in general matrix was tested applying three different temperatures, 15°C, 30°C and 45°C. Simulations applied with hydrogen peroxide were only analysed by LC-MS/MS and the results are summarised in Table 49. The results were fitting to results of previous simulations. The detected DBPs were limited to three different aldehydes and one ketone (acetophenon). DBPs detected at highest concentration was acetaldehyde with 2.6 µg/L at 45°C. Further aldehydes detected were propanal and benzaldehyde.

The sum of detected DBPs in simulations applied with chlorine and sorted by DBP classes is shown in Figure 27. The influence of reaction temperature in simulations with chlorine as a.s. was significant. For all DBP classes, the concentration continuously increased with increasing temperature. HAAs were the DBP class observed at highest concentrations and further DBP classes observed at significant concentrations were aldehydes, HALs, THMs and HANs. With respect to the total DBP concentration, the increase from 15°C (approx. 300 µg/L) to 30°C (approx. 900 µg/L) was bigger than from 30°C to 45°C (approx. 1100 µg/L). Interestingly, at 15°C only HAAs were observed at significant concentrations, indicating that in the general matrix treated by chlorine HAAs are formed easily (kinetic reaction product), while the formation of the other DBP classes needs more activation. However, this is only a general assumption, as a detailed assessment would only be possible knowing the reaction routes for the particular DBPs. At 30°C, HAA concentration increased but also the other DBP classes were observed, indicating that at 30°C more different chemical reactions were occurring in the system. The relatively low increase of DBP concentrations from 30°C to 45°C should be regarded considering the previous results observed by variation of chlorine and TOC concentrations, indicating that the TOC concentrations was a limiting parameter within the parameter matrix of the present simulations. This was confirmed by the results of the temperature variation, as increase of temperature would not be effective in case a reaction substrate was not present at sufficient amounts.

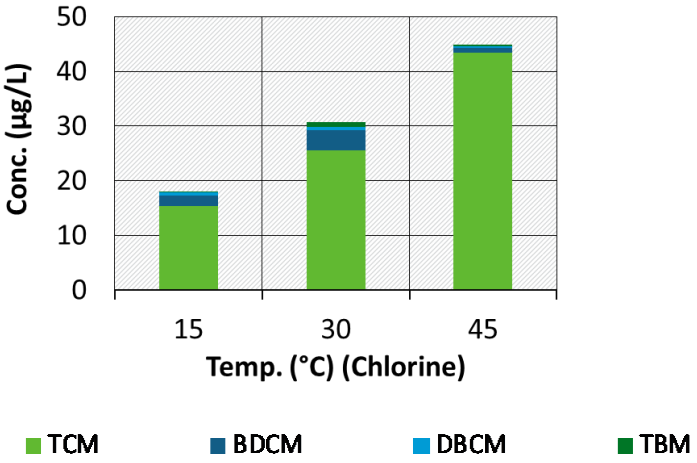
Figure 27: Sum concentration of DBP classes generated at different reaction temperatures for hypochlorite



Source: own illustration, diagram with experimental results

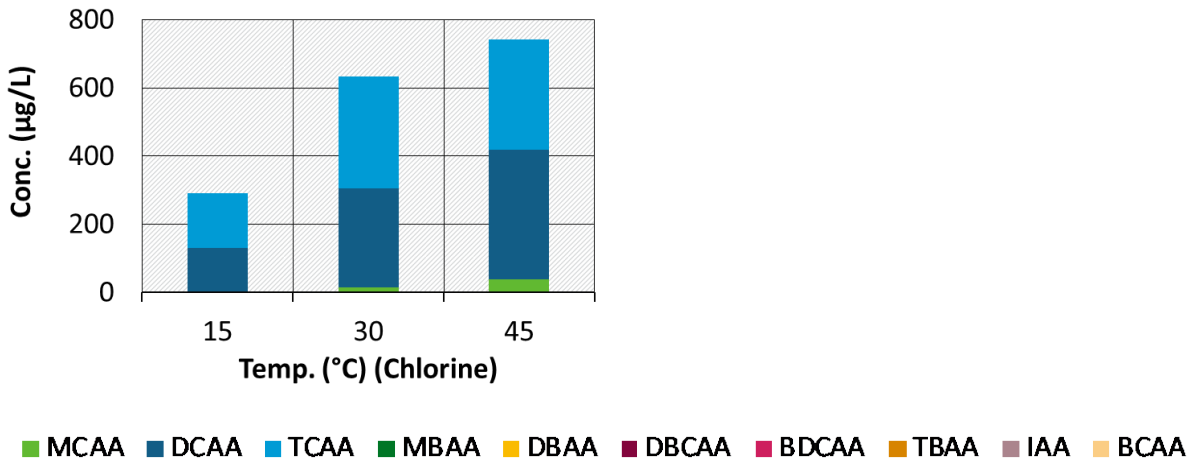
Detailed information on formed THMs and HAAs in the simulations with variation of temperature are shown in Figure 28 and Figure 29. As detected in previous simulations also at different temperatures only few substances were dominating the total amount of the generated DBPs. TCM was by far the dominating representative of THMs and for HAAs mostly TCAA and DCAA were observed. The ratio of TCAA and DCAA was not significantly changing for the different temperatures. Furthermore, high concentrations were again determined for acetaldehyde and trichloroacetaldehyde (see Table 45 and Table 46), and brominated DBPs were found only at low concentrations.

Figure 28: Trihalomethanes (THMs) generated at different reaction temperatures in general matrix and hypochlorite



Source: own illustration, diagram with experimental results

Figure 29: Haloacetic acids (HAAs) generated at different reaction temperatures in general matrix and hypochlorite



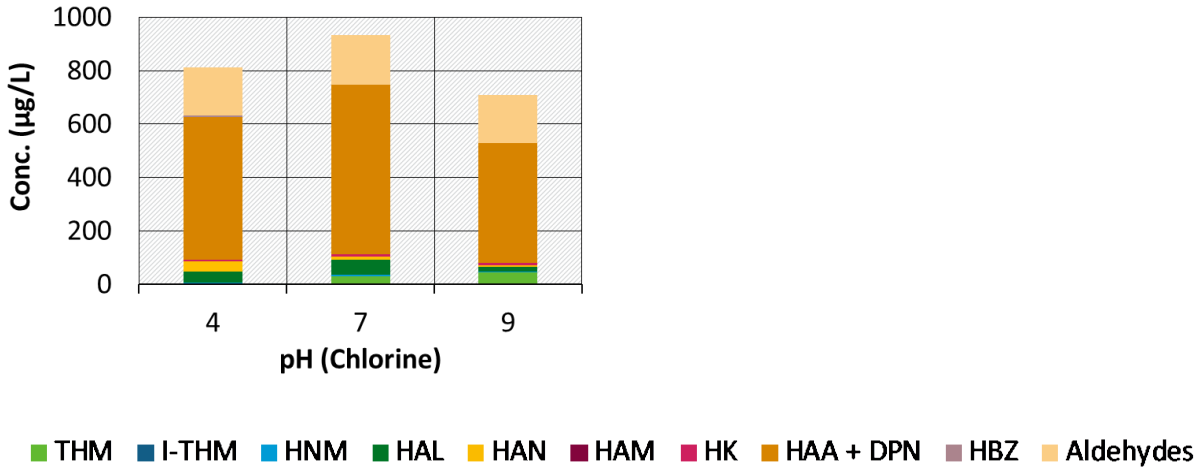
Source: own illustration, diagram with experimental results

Variation of reaction pH value

In contrast to the simulations with the swimming pool matrix, where a variation of pH was not reasonable with respect to expected real disinfection conditions, pH was varied as parameter in simulations with the general matrix. The simulations applied with hydrogen peroxide were only analysed by LC-MS/MS and the obtained results were comparable to corresponding previous simulations. Only low concentrations of two aldehydes were determined, with a maximal value of 3.9 µg/L for acetaldehyde at pH9.

The detected DBP amounts are summarized in DBP classes in Figure 30 for the simulations applied with chlorine. The pH value had no significant influence on the total DBP formation. Highest DBP amount was observed at pH7 (approx. 900 µg/L) followed by pH4 (approx. 800 µg/L) and pH9 (approx. 700 µg/L). These total values were mainly determined by the total values of HAAs as the main DBP class. The amount of aldehydes, as the second highest one, were not changing with the pH. Systematic influence of pH value was observed for DBP classes observed at significant but lower concentrations. The concentrations of HANs and HALs were decreasing with increasing pH value, while the concentration of THMs was increasing, as already described by Hansen et al (2012 and 2013). Regarding the reactivity of HOCl/OCl^-, HOCl has the significantly higher reactivity, therefore generally higher DBP formation was expected at lower pH values. Obviously, the influence of the pH is not limited to influence of the chlorine reactivity. One reason for the observation could be the long incubation time of 24h compensating the lower activity of OCl^-. Besides the chlorine reactivity, pH may influence (accelerate or slow down) reaction steps leading to generation of certain DBP families or influence the reactivity of the matrix, however this can only be assumed. Finally, for both pH4 and pH9 a significant shift to neutral pH was observed at the end of the incubation time as pH6.4 and pH8 were determined. Obviously, reaction products formed during the simulation were influencing the original pH and the corresponding results with respect to pH variation.

Figure 30: Sum concentration of DBP classes generated at different pH values for hypochlorite



Source: own illustration, diagram with experimental results

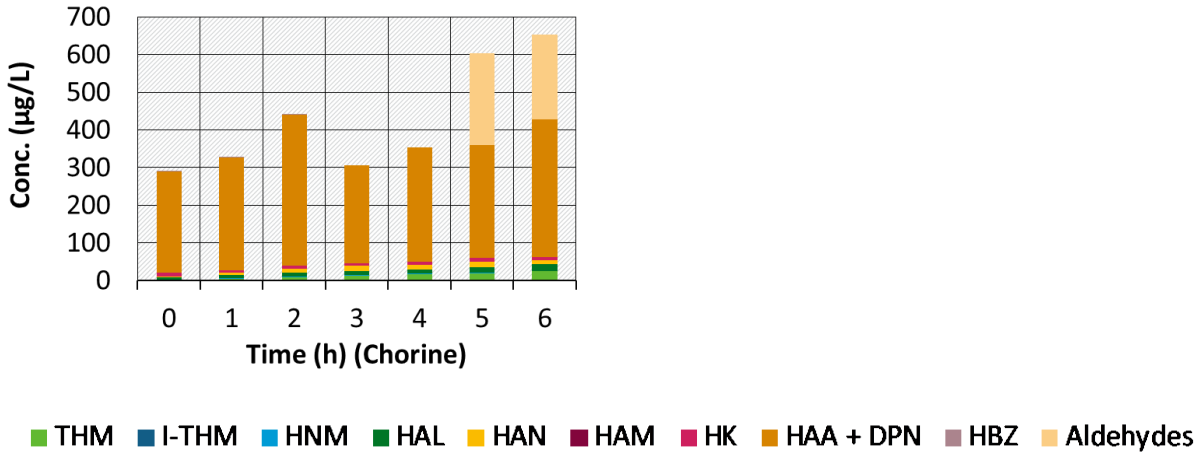
Regarding the single substances, the same were dominating the total DBP amounts as in previous simulations with the general matrix. TCM was the dominating representative of THMs and TCAA and DCAA the representatives of HAAs detected at highest concentrations. Among the aldehydes it was again acetaldehyde. Although the total amount of aldehydes was not changing with pH, it is remarkable that the concentration of acetaldehyde was slightly decreasing with increasing pH, while the concentration of benzaldehyde, the aldehyde with second highest concentration, was increasing with increasing pH (see Table 46).

Variation of time (kinetic experiment)

The influence of reaction time on the DBP formation was, as for the swimming pool matrix, monitored for the initial 6 h of incubation time. Analysis of simulations applied with hydrogen peroxide by LC-MS/MS did not show any significant time dependency, which could be expected regarding the generally low levels of DBP found in the simulations applied with hydrogen peroxide. The results are summarized in Table 51. It must be pointed out that the detection of monobromoacetic acid for all time points at the same concentration level of 6-7 µg/L was obviously caused by a contamination, as no monobromoacetic acid and also no other brominated DBPs were detected in any simulation applied hydrogen peroxide.

DBPs detected in simulations applied with chlorine are summarised in Figure 31. Generally, mainly formed DBPs were HAAs and aldehydes for the later sampling time points. However, the data showed similar problems as already observed in the kinetic experiment with the swimming pool matrix and allowed only limited interpretation. High amounts of HAAs were observed already at the initial sampling time point and a clear time dependency was not present for the main DBP classes observed, HAAs and aldehydes. Furthermore, aldehydes were observed at quite high amounts of approx. 250 µg/L but only in the last two sampling time points. These results were not easy to interpret but a not parallel progress of the chemical reactions in the individual samples set up for every sampling time point could be a reason. Considering the evaluation shown in Figure 24, it is also possible that with progressing reaction time the chlorine:TOC ratio is decreasing in the mixture, as chlorine is reacting multiple times with the same carbon atom (e.g. di- tri-halogenation). This could also explain the occurance of aldehydes at later reaction times.

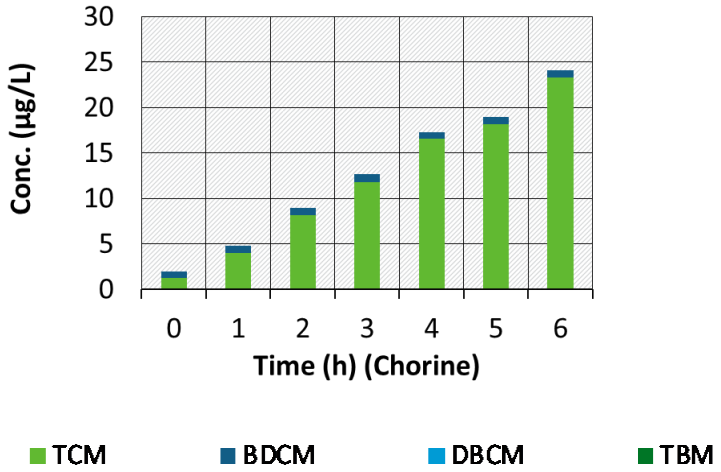
Figure 31: Sum concentration of DBP classes generated after different reaction times for general matrix and hypochlorite



Source: own illustration, diagram with experimental results

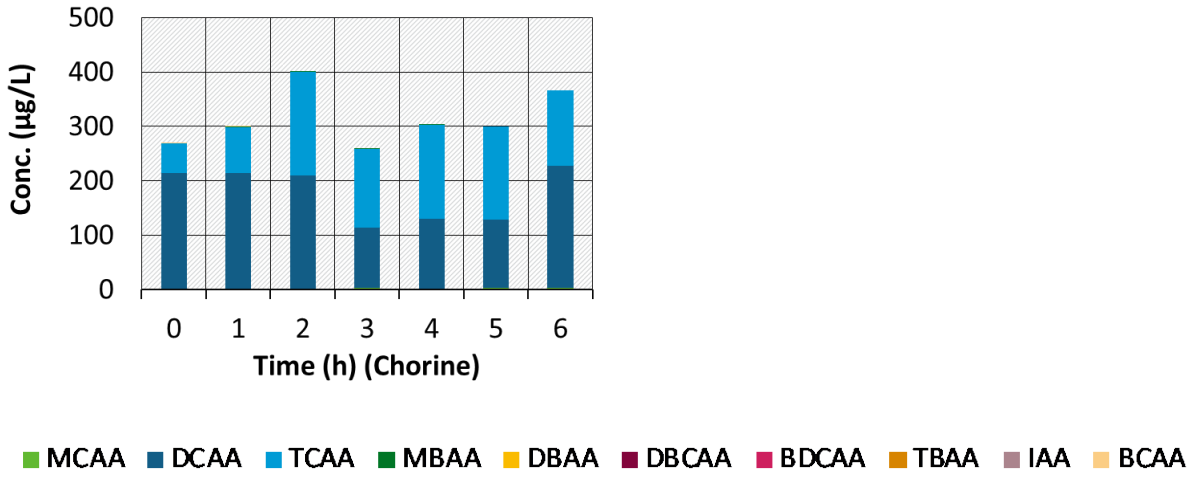
Regarding the single substances of THMs and HAAs, a clear increase of TCM with time was observed (Figure 32). As in the kinetic experiment with the swimming pool matrix, the reason may be that THMs are final reaction products of the DPB formation and thus were behaving less complicated in the reaction mixture. Values for DCAA and TCAA were summarized in Figure 33 and show that no interpretation was possible with respect to time dependency of their formation.

Figure 32: Trihalomethanes (THMs) generated after different reaction times for general matrix and hypochlorite



Source: own illustration, diagram with experimental results

Figure 33: Haloacetic acids (HAAs) generated after different reaction times for general matrix and hypochlorite (no interpretation of time dependency possible)



Source: own illustration, diagram with experimental results

6.6.4 Laboratory simulations with general matrix on surfaces

The reaction conditions of disinfections on surfaces differ significantly from conditions in solution. The main difference was the extremely reduced volume of water as a solvent. In the simulations performed within the present study, the volume added in the disinfection simulations on surfaces was 1 mL, which was used for the application of the respective a.s.. In contrast to the reduced water volume, the amounts of a.s. in the simulations were in the same range like in the simulations in solution. The standard amount of chlorine in the simulations on surfaces was 5 mg, compared to 15 mg in the simulations in solution (considering the volume of 300 mL as used for subsequent LC-MS/MS analysis) and the standard amount of TOC were 2 mg, compared to 0.3 mg in the simulations in solution (considering the volume of 300 mL as used for subsequent LC-MS/MS analysis). Thus, comparable amounts of reactants, a.s. and TOC, but only a very low volume of solvent, were present in the simulations. However, for work-up and analysis, further 30 mL water including the quenching substance were added at the end of the incubation time, which was inevitable for analysis but may have influenced the results. The DBP concentrations in the simulations on surfaces are related to this volume and consequently, in case of the same concentration, the total DBP amounts in the simulations on surfaces are by a factor of 10 lower compared to the simulations in solution with a final volume of 300 mL. On the other hand, the significantly shorter simulation time of 2h for the surfaces versus 24h for the solutions needs to be considered when the results are directly compared. The analysis of the formed DBPs was even more challenging compared to the analysis of the simulations performed in solution. The analysis by LC-MS/MS was again facing high concentrations of the general matrix in the samples, while the sample work-up for GC/MS analysis was problematic due to the headspace in the simulation vessels. Although the vessels could be sealed gas tight and the addition of both, the application solution and the extraction agent, were performed by syringe through a septum, loss of volatile DBPs in the headspace, not solubilised by the extraction agent, cannot be excluded.

The treatment of general matrix on surface with chlorine and chloramine T led in both cases to formation of DBPs within the analytical scope of the present study. The results are summarised in Table 52 - Table 59. The total amount of DBP after treatment with chlorine was approx. one to two orders of magnitude higher compared to the treatment with chloramine T. Although both a.s. are chlorinating agents, their reactivity significantly differs (Gottardi, 1992). Similar to

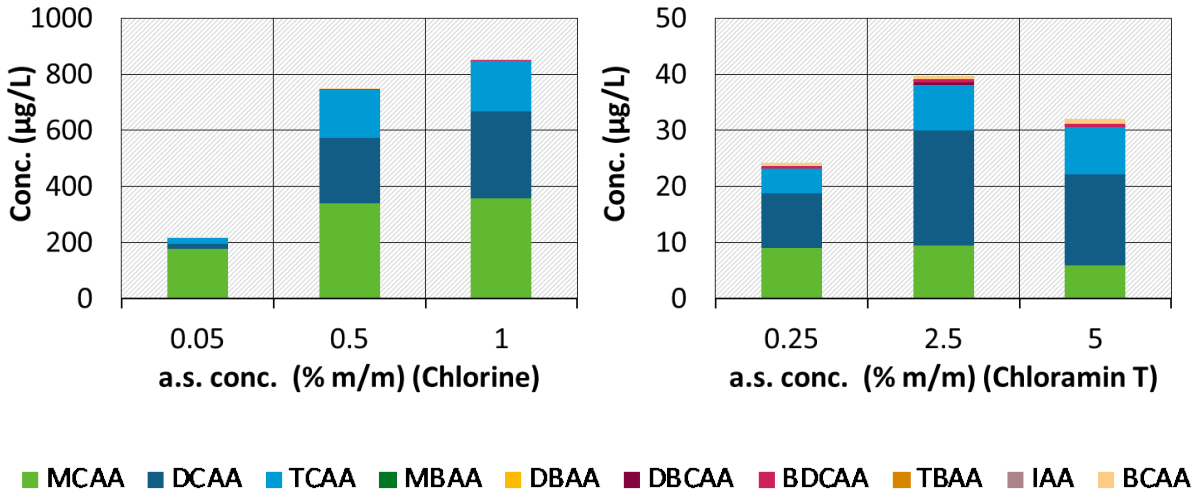
simulations with general matrix in solution, the total amount of formed DBPs was dominated by only few different substances. Treatment with chlorine led to the formation of high amounts of dalapon, found only at minor amounts in the corresponding simulations with general matrix in solution. Highest amount with 747 µg/L was observed for the high a.s. concentration. Further main DBPs were chlorinated HAAs also observed at highest amounts for the high a.s. concentration. In contrast to the simulations in solution MCAA (359 µg/L), representing a minor DPB in solution, was found at highest concentrations followed by DCAA (307 µg/L) and TCAA (181 µg/L). Both findings, the occurrence of dalapon as main DBP and the tendency to lower chlorination degrees of the HAAs, indicated that the differing reaction conditions, most probably low volume of water and shorter reaction time, led to formation of DBPs not observed as main products in the simulations in solution. In the simulations in solution, these DBPs were assumed to be intermediate DBPs, reacting further and thus being not detected or only at minor amounts. Only detected THM was TCM with maximal concentration of 80 µg/L in simulation with high a.s. concentration. After treatment with chloramine T, main detected DBPs were the three chlorinated HAAs MCAA, DCAA and TCAA. The exceptionally high value for DCAA in the simulation with high TOC was the result of a subsequent remeasurement and cannot be compared to the values of original measurements. Considering this, highest concentrations were observed for DCAA (21 µg/L) followed by TCAA (20 µg/L) and MCAA (18 µg/L), both in the simulation with high TOC concentration. All other DBP, including THM and dalapon, were observed at concentrations not exceeding 3 µg/L. Brominated DBPs were observed after treatment with both a.s. always at minor amounts. Interestingly, more brominated DBP were found in simulations applied with chloramine T. Also, this observation indicates differences between the reactivity of chloramine T and chlorine.

Variation of the chlorine and chloramine T concentrations

Three different a.s. concentrations were applied to test the influence of the a.s. concentration on DBP formation. It should be pointed out that the a.s. concentration in the simulations in solution refers to the total volume of a simulation experiment (e.g. 300 mL for subsequent LC-MS/MS analysis), while in the simulation on surfaces, the concentration is given for the solution (1 mL) applied to the surface. Figure 34 and Figure 35 summarise the amounts of detected HAAs and THMs in simulations with different a.s. concentrations. A presentation of the total DBP amount sorted by DBP classes was skipped, as in Figure 34 and Figure 35 only dalapon in simulations with chlorine as a.s was missing as a relevant DBP. The amounts of HAAs and THMs were increasing with increasing a.s. amounts with exception of HAAs for the highest chloramine T concentration, where HAA amounts are highest for the middle a.s. concentration. For both, HAAs and THMs, the significantly higher DBP amounts after treatment with chlorine clearly indicated the higher reactivity of chlorine compared to chloramine T, which is known and described for example by W. Gottardi (Gottardi, 1992). The reason are the different chemical species responsible for the reactivity. Within the pH range determined in the simulation mixtures of pH 6-7, the dominant reactive species are HOCl for chlorine and $RNCl^-$ for chloramine T. Both a.s. formed the same HAAs, the solely chlorinated MCAA, DCAA and TCAA. This was corresponding to the finding of TCM as only THM after the application of chlorine and also to the simulations with general matrix in solution, indicating that the matrix was determining the type of DBPs formed. Only for the lowest chlorine concentration aldehydes were detected, with acetaldehyde and propanal at 20 µg/L and 8 µg/L respectively. A possible explanation is, that the aldehydes undergo further reactions at higher chlorine concentrations, which were stopped due to lack of chlorine at lowest chlorine concentration. Similar was observed in experiments with general matrix in solution, where aldehydes were observed at high concentrations for high TOC:a.s. ratios. However, simulations in solution and on surface should be compared with care as

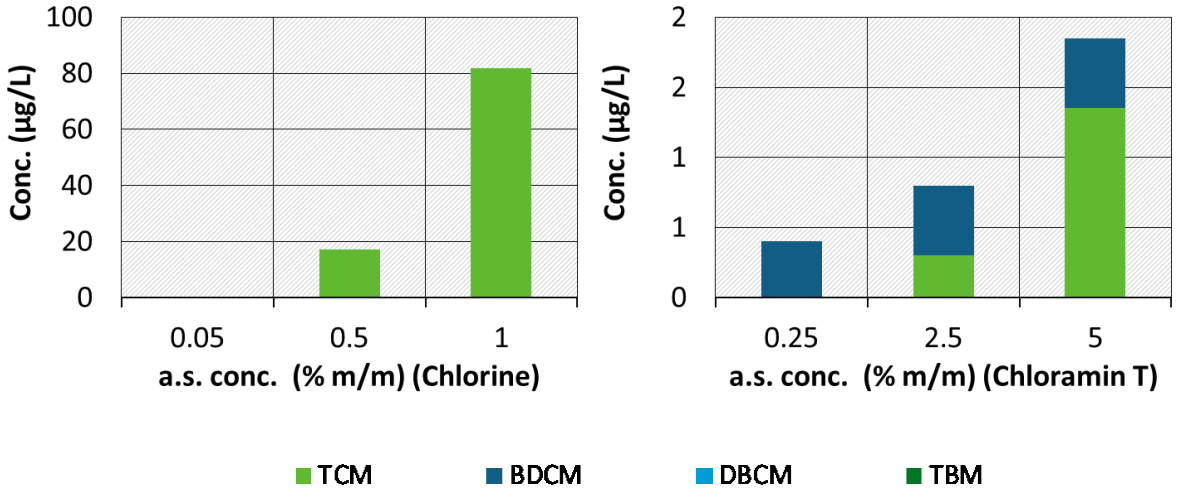
reaction conditions are quite different in both cases and analytical insecurities were present to some extent.

Figure 34: Haloacetic acids (HAAs) generated at different hypochlorite (left) or chloramine T (right) concentrations



Source: own illustration, diagrams with experimental results

Figure 35: Trihalomethanes (THMs) generated at different hypochlorite (left) or chloramine T (right) concentrations



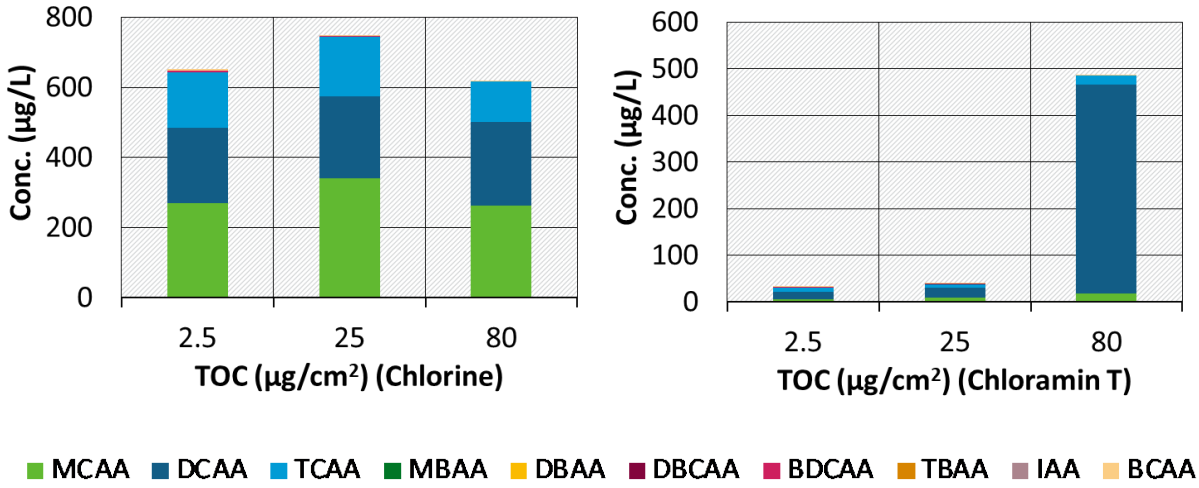
Source: own illustration, diagrams with experimental results

Variation of total organic carbon (TOC) concentrations

In the simulations of disinfection uses on surfaces, the concentration of TOC was related to the surface of the test vessels and is given as µg/cm². Three different concentrations were tested and the results for THMs and HAAs are shown in Figure 36 and Figure 37 The samples with the highest TOC concentrations for GC-MS/MS analysis could not be worked-up with the method applied for all previous analyses, as the aqueous residue resulting after the extraction of the simulation vessel could not be filtrated. Therefore, no values were available for THMs at the highest TOC concentration. The samples of the simulation with chloramine T and the highest TOC concentrations for LC-MS/MS analysis needed to be remeasured after a day of storage and resulted in extraordinary high value for DCAA. Consequently, the values cannot be compared to

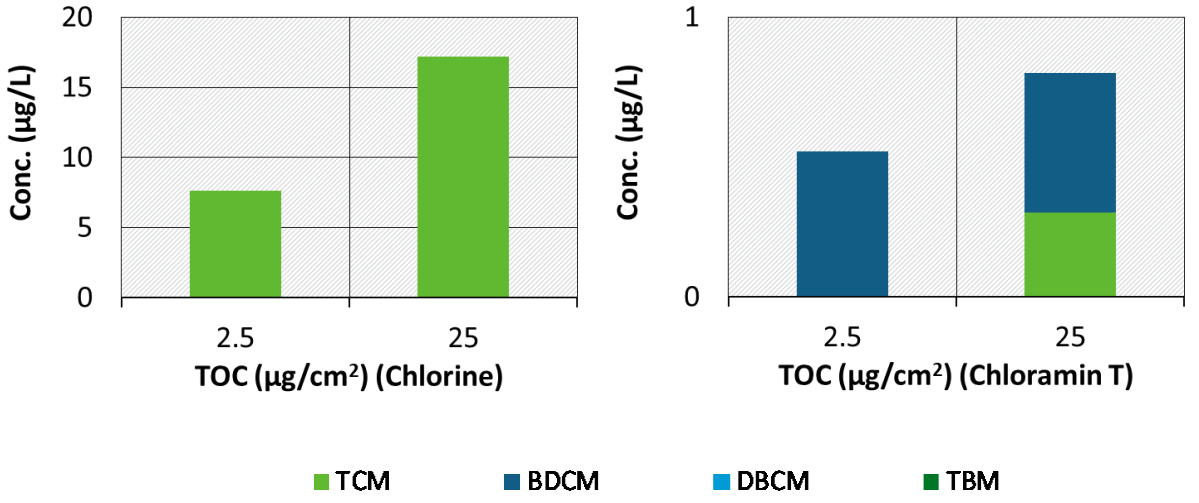
the values of the other TOC concentrations. The observation showed that chloramine T was not properly quenched by ascorbic acid and reacts further in the worked-up samples. Excluding these samples, the variation of TOC concentration did not significantly influence the amount and composition of generated HAAs for both chlorine and chloramine T. It seems that at the given simulation conditions for surface disinfection neither a.s. nor TOC were limiting factors for HAAs formation within the incubation time of 2h. This can be understood considering the low amount of a reaction medium (solvent) in this simulation set-up, which limited the reaction by the solubility and thus availability of TOC in the low volume. The amounts of both DBP classes, HAAs and THMs were again higher applying chlorine as a.s. confirming the results of simulations with different a.s. concentrations. The amount of detected THMs in the simulations with chloramine T was very low.

Figure 36: Haloacetic acids (HAAs) generated using different TOC concentrations for hypochlorite (left) or chloramine T (right) as a.s



Source: own illustration, diagrams with experimental results

Figure 37: Trihalomethanes (THMs) generated using different TOC concentrations for hypochlorite (left) or chloramine T (right) as a.s



Source: own illustration, diagrams with experimental results

Variation of time (kinetic experiment)

In disinfection simulations on surfaces, the influence of reaction time on the DBP formation was monitored for the complete incubation time of 2h in intervals of 20 min. A systematic time dependency for DBP formation could be observed neither for HAAs or THMs nor for chlorine or chloramine T as a.s.. Therefore, no graphic presentation of the results was prepared. Already for the 0h samples significant amounts of the monitored DBP were detected, indicating that either an immediate quench of the reaction was not successful or problems with analytical background values occurred. However, background values should have been observed also in all other variations of the disinfection simulations on surfaces, which was not the case at least not at these high concentrations. Possible background values are addressed in detail in chapter 6.6.1.1. Therefore, it is assumed that under given conditions an immediate quench of the reaction was not successful and the reaction continued at least for some time during the sample processing and analysis. Although the main intention of the kinetic experiment was not achieved, the analysis showed that again the same limited amount of different DBPs was observed in the simulations with general matrix on surfaces, confirming these results. This also included high values of dalapon after application of chlorine (see Table 55). Furthermore, in most cases the measured DBP amounts were in the same range as observed in earlier simulations with general matrix on surfaces, showing after treatment with chlorine DBPs amounts being more than one order of magnitude higher compared to chloramine T treatment. This was different for samples after treatment with chloramine T and reaction times of 40 and 60 min. In these samples very high values of HAAs, especially DCAA are found. The samples were, same as in the simulation with chloramine T and the highest TOC concentrations, remeasured after one day of storage. The reason for the remeasurement however, were very high values in the original measurements (531 µg/L and 270 µg/L DCAA after 40 and 60 min respectively), leading to results outside of the calibration and also not fitting to the results of the other time points. Looking closer at the results of these three samples revealed another mutuality. Only in these samples 2,6-dichloro-1,4-benzoquinone was detected. The observed amounts of 2 µg/L - 5 µg/L were not very high but significant with respect to the analytical method applied. Although unexpected, the measured values did not look like random errors. Especially, because all three samples were measured in well correlating duplicates and the series of samples for the kinetic experiment were set up at the same time using exactly the same components (solutions etc.). There is no obvious reason to explain the differing results in these three cases, but it was an indication, that either a main parameter influencing the DBP formation was not considered and controlled or that small experimental differences in the individual samples had a significant impact on the simulation results.

6.6.5 Genuine disinfection samples

The results of the analyses of pool and spa water also have been published with more details in Usman et al., 2022

6.6.5.1 Water samples from open-air swimming pools

The outdoor pool site used drinking water from the local drinking water plant as filling water. After filtration, disinfection by chlorination with chlorine gas was carried out and finally, pH correction of the treated water was performed. The outdoor swimming site consisted of 3 pools swimming pool, non-swimmers pool and small children's pool. The non-swimmers pool and the small children's pool had a joined treatment system for the pool water. The swimming pool had its own treatment system. The sampling parameters are summarised in Table 18. The investigated swimming pools could only be operated with a limited number of visitors due to corona restrictions, which could be a reason for the moderate levels of TOC.

Table 18: Parameters at sampling of open-air swimming pool water

	Open air swimming pool			
Pools	Non-swimmers pool	Children's pool	Swimming pool	Fill-up water
Sampling time	15.00-17.30	15.00-17.30	15.00-17.30	
No. of visitors*	max. 600	max. 600	max. 600	
Free chlorine [mg/L]	0.41	0.43	0.41	0.07
Water temperature [°C]	24.40	24.2	24.4	5.5
TOC [mg/L)	1.2	<1.0	1.4	1.3
pH value	7.01	7.05	7.01	7.9
Redox potential [mV]	809	805	809	

* max. 4000 without corona restrictions

The analytical results of DBP determination in the open-air swimming pools are shown in Table 60 and Table 61. DBPs from the most DBP classes were detected in the swimming pool water. This result was similar to the observations made in the simulations with artificial swimming pool matrix applied with hypochlorite. The highest amounts were detected for HAAs followed by the DBP classes of HALs and aldehydes. Significant concentrations were also observed for HKs, HANs and THMs, while HAMs, HNMs and I-THMs were present at low levels. THMs were found at lower ratios compared to the results in the simulations experiments. As could be expected in absence of bromide sources and as was observed in the simulations with the general matrix, chlorinated DBPs were dominating by far from all halogenated DBPs. Brominated substances were detected only at low or very low levels. Regarding single substances found at highest amounts, mostly the same substances were also observed in the laboratory simulations at highest levels, TCM for the THMs, trichloroacetaldehyde for HALs, TCAA and DCAA for HAAs and acetaldehyde for aldehydes. A large proportion of the DBPs was already present in the filling water therefore the main part of the detected DBPs was not due to the bather's discharge. An inquiry with the local drinking water producer revealed that recently the drinking water used as filling water was more chlorinated than usual. Consequently, the detected DBPs cannot be used to examine a typical contamination of chlorinated swimming pool water with DBPs, but rather an example of chlorinated drinking water. Differences between the single pools with respect to

detected DBPs were not significant or are superimposed by the domination of DBPs originating from the filling water.

6.6.5.2 Water samples from a thermal spa

The thermal SPA used two water sources. Hamam and the cold-water pool were filled using drinking water from the local drinking water. The filling water for these pools was not analysed. The treatment of the filling water was carried out by using flocculation followed by a filtration. Afterwards disinfection by chlorination with hypochlorite solution was performed and the pH was corrected. The other pools, hot water pool, the sauna pool, the main pool, the sitting pool and the whirlpool, were filled with thermal water. Before use, the thermal water was pre-treated by ultrafiltration and chlorination, followed by oxygenation to remove sulfur and manganese. After a subsequent filtration, the thermal water was ozonated and once again filtered. The pre-treated themal water was stored and used as filling water for the thermal water pools. In service, flocculation and ozonation were performed, followed by filtration and chlorination with chlorine gas. The sampling parameters are summarised in Table 19. The investigated swimming pools could only be operated with a limited number of visitors due to corona restrictions, which could be a reason for the moderate levels of TOC.

Table 19: Parameters at sampling of thermal spa water

	Thermal spa							
Pools	**Fill-up water**	**Hot water pool**	**Sauna pool**	**Main pool**	**Sitting pool**	**Hamam**	**Cold water pool**	**Whirl pool**
Sampling time		12.30-15.00	12.30-15.00	12.30-15.00	12.30-15.00	12.30-15.00	12.30-15.00	12.30-15.00
No. of visitors*		max. 900	max. 900	max. 900	max. 900	max. 900	max. 900	max. 900
Free chlorine [mg/L]	0.89	0.64	0.36	0.48	0.39	0.53	0.49	1.58
Water temperature [°C]	39.3	36.8	33.2	33.5	33.4	26.3	22.60	36.1
TOC [mg/L]	< 0.5	0.98	1.3	1.0	0.95	1.0	2.4	2.8
pH value	6.99	7.15	7.13	7.13	7.13	7.19	7.13	7.16
Redox potential [mV]	759	811	739	766	758	791	774.00	773

* max. 2000 without corona restrictions

The analytical results of DBP determination in the thermal spa pools are shown in Table 62 and Table 63. Significant differences regarding the formed DBPs were observed between the pools filled with drinking water, hamam and cold-water pool and the pools filled with thermal water. In the pools filled with drinking water, results were similar to the results of the open-air swimming pool. The total concentration of detected DBPs was in the range of 100 µg/L – 200 µg/L and chlorinated DBPs were mainly found. The main difference was the changed ratio of THMs and HAAs. In contrast to the open-air swimming pools, in the hamam and the cold-water pool THMs were found at higher concentrations and were the main DBPs found in the cold-water pool. The different ratios of THMs and HAAs were probably caused by the different chlorination techniques used in the open-air swimming pools and hamam and cold-water pool. Among single DBPs, trichloromethane and trichloroacetic acid were found at highest concentrations within the DBP classes of THMs and HAAs. Comparing the two pools filled with drinking water, the total amount of DBPs was higher in the cold-water pool. This was correlating well with the higher TOC loading found in the cold-water pool indicating that the TOC content has a higher influence on DBP formation than the temperature. Besides the DBP classes of THMs and HAAs, also higher concentrations of HALs, HANs and HKs were found in the cold-water pool. Among HANs, different representatives were detected at similar concentrations, while for HALs and HKs mainly trichloropropanon and trichloroacetaldehyde represented the detected DBP amount.

In the pools filled with thermal water, the total amounts of detected DBPs showed a broad range between approx. 150 µg/L in the hot-water pool and approx. 450 µg/L in the whirlpool. Only for the whirlpool, the higher DBP concentrations correlated to a higher TOC concentration of 2.8 mg/L compared to approx. 1 mg/L found in the other pools filled with thermal water. As in the thermal filling water only low total concentrations of DBPs were found, the detected DBPs could be attributed to the input by the bathers. In the thermal filling water, 2.5 mg/L bromide is present. The presence of bromine causes a significant formation of brominated DBPs. Brominated and mixed chlorinated-brominated substances represented the main part of DBPs detected in the thermal water pools. Among THMs, TBM was mostly found at highest concentrations, followed by DBCM and for HANs DBAN was the dominant compound. Within the HAAs, DBAA and the mixed chlorinated-brominated DBCAA were found at highest concentrations. TBAA was found at lower levels and a reason for this could be the low stability of TBAA (Richardson et al., 2008; Sfynia et al., 2020). This was in good agreement with high levels of TBM, as it was a product of TBAA decomposition. Highest total DBP concentrations in the rage of 400 µg/L - 500 µg/L were determined in the sauna pool and the whirlpool with THMs, HAAs and HANs as dominating DBP classes. While comparable concentrations of THMs and HAAs were also determined within the laboratory simulations using swimming pool matrix, comparably high concentrations of HANs were not validated by the simulations as only observed for the combination hypobromite as a.s. and high TOC concentration. The high concentrations of HANs in in the sauna pool and the whirlpool was also remarkable within the five thermal water pools. Regarding the DBPs detected in the thermal filling water, the formation of HANs was largely due to human exposure and as the same water was used for all thermal pools the observed difference clearly showed that formation and amount of particular DBPs will depend on individual factors of a disinfection process, which are not always easy to distinguish. In this context the results confirmed similar observations made during the laboratory simulations.

6.6.5.3 Water samples from industrial cooling systems

Samples originating from 16 cooling systems at 10 different facilities were analysed for DPB concentrations. Available parameters of the cooling systems are summarised in Table 20. All of the sampled cooling systems belong to metalworking industry except system F21 that belongs to

food industry. A detailed assessment of the systems is not possible, as important information about the systems like volumes and volume flows was not available. Furthermore, considering the results of previous analyses in the present study, TOC concentration is an important parameter for the generation of DPBs but also the particular composition of the TOC has a significant impact on DBP formation. This was not known for the samples. Additionally, in the most sampled systems chlorine dioxide was applied as a.s. for disinfection, partially combined with other a.s.. Chlorine dioxide acts primary as an oxidation agent and the chlorination reactivity is lower compared to hypochlorite. Furthermore, additives for corrosion protection and/or control of water hardness were also applied influencing DBP formation of each cooling system individually. Therefore, a direct comparison with the laboratory simulations performed within the present study was not possible. Only in the systems HoA and MKW with hypochlorite and hydrogen peroxide the same biocidal a.s. as in the laboratory simulations were used. Nevertheless, the analysis for DBPs showed some interesting results. Generally, it can be pointed out, that the "Contamination/matrix loading", stated by the partner that provided the samples, as well as the TOC determined in the samples within the present project were not necessarily correlating with the amount of DBPs. The reason could be either that the particular matrix loading or TOC was not relevant for DBP formation or that generated DBP were not within the analytical scope of the present study. Furthermore, the total DBP amounts detected in the cooling systems were low to moderate. The results are summarized in Table 64 - Table 66 (GC-MS analyses) and Table 67 - Table 69 (LC-MS analyses).

Table 20: Basic parameter of the sampled industrial cooling systems

System code	System usage	System origin	System type (open/closed)	Fill-up water	Operating temp.	pH	Contamination/matrix loading acc. to company	TOC [mg/L]	Applied biocide
F21	Process cooling	Food (sugar) industry	Open	Reprocessed by user	20 - 45	8.3	High (organic process additives)	1.2 – 1.4	Ozone/Chlorine dioxide 7% (in-situ)
KKA 1	Strand cooling	Aluminium industry	Open	Tap water	25 - 60	8.3	Low	< 0.5	CMIT/MIT 3:1 1.5%/ Chlorine dioxide 7% (in-situ)
RKW-SM	Heat transport	Steel industry	Open	Service water	20 - 30	8.4	Very low	0.98	Chlorine dioxide 7% (in-situ)
HoA	Machinery cooling	Steel industry	Open	Service water	20 - 35	8.0	Low	5.23	Sodium hypochlorite 13%
SpW 1/2, 3, 4	Strand cooling	Steel industry	Open	Service water	25 - 35	5.5 (1/2), 7.3 (3), 8.3 (4)	Very high (inorganic, organic, leakage from other cooling systems)	9.8 (1/2), 11.4 (3), 10.8 (4)	Chlorine dioxide 7% (in-situ)
Ko1, 2, 3, 4	Component cooling	Steel industry	Closed	Condensate	35 - 45	10.1 – 11-2	Very low	43.5 – 75.2	Chlorine dioxide 7% (in-situ)
StGas	Flue gas scrubber	Steel industry	Open	Service water	35 - 45	7.2	Very high (inorganic, metal dust)	18.2	Chlorine dioxide 7% (in-situ)
KKW	Machinery cooling	Steel industry	Open	Service water	20 - 30	8.3	High (alloying materials)	n.d.	Chlorine dioxide 7% (in-situ)
MKW	Component cooling	Steel industry	Closed	Condensate	25 - 35	7.7	Low	28.3	Hydrogen peroxide 35%
ML 1, 2	Component cooling	Steel industry	Closed	Reverse osmosis water	35 - 45	9.4 (1), 9.0 (2)	Usually low Situational high (corrosion products and glycol)	72.9 (1), 30.7 (2)	Chlorine dioxide 7% (in-situ)

The systems HoA and MKW with hypochlorite and hydrogen peroxide showed similar results as the corresponding laboratory simulations. Almost no DBPs were determined in samples from system MKW treated by hydrogen peroxide. Only small amounts of THMs and HAAs, all below 1 µg/L were detected, despite a significant TOC concentration of nearly 30 mg/L. Interestingly, all detected DBPs were mixed chlorinated-brominated substances. In the system HoA, treated by hypochlorite, TOC concentration of 5 mg/L and bromide concentration of 2.7 mg/L was measured. These values were corresponding well with the determined DBPs. Mainly THMs and HAAs were found, concentrations > 1 µg/L were also observed for HALs, HANs and non-halogenated aldehydes. Both chlorinated and brominated compounds were detected. Highest concentrations > 10 µg/L were measured for TCM, BDCM, DCAA and TCAL and the total DBP concentration was in the range of 100 µg/L. The detected DBPs could be mostly attributed to the disinfection process, as with exception of TBM no or significantly lower concentrations of the corresponding DBPs were found in the filling water.

Among the cooling systems disinfected by chlorine dioxide, KKA 1 was a remarkable example. Although the matrix loading was stated as low, which was also confirmed by the low TOC concentration (< 0.5 mg/L), in this system the highest DBP concentrations of all analysed cooling systems were detected. Total amount of DBPs reached nearly 300 µg/L. HAAs were dominating the DBPs reaching a concentration of approx. 200 µg/L and the main representative of HAAs was DBAA with a value of >120 µg/L. Significant were also the concentrations of HANs with a sum of >50 µg/L, while THMs were less relevant and detected at a total concentration of 13 µg/L. While the occurrence of brominated DBPs could be explained by the bromide concentration of 3.6 mg/L, the general occurrence of DBPs at high concentrations, regarding the other analysed cooling systems, was noticeable. Considering the available information, it was assumed that the addition of chlormethylisothiazolinon/methylisothiazolin-one (CMIT/MIT) as additional biocidal a.s. was responsible for this result. Among the cooling systems disinfected by chlorine dioxide, CMIT/MIT was added only in KKA 1 and the present N-source in CMIT/MIT could explain the high HAL concentrations. The detailed reason for the addition of CMIT/MIT in this particular cooling system in not known, but generally the disinfection treatment is optimized for each system and it is assumed that in this case the addition of CMIT/MIT was promoting the disinfection process. In contrast to the laboratory simulations, where the matrix loading was assumed to be the main source for DBPs in this particular case the mixture of applied biocide a.s. seemed to source for DBP formation.

Interesting was also the comparison of systems Ko 1-4 and ML 1, 2. In both systems, the matrix loading was stated to be low, but the TOC concentrations of up to >70 mg/L were the highest of the analysed cooling systems. For disinfection, only chlorine dioxide at same concentration was used and the same corrosion protection. Regarding these parameters the systems were quite similar. This was also the case regarding the detected DBPs. In both systems, THMs are dominating with TCM as main representative and only HAAs were also detected at relevant concentrations. However, the total amounts of detected DBPs, especially THMs, were differing significantly. In Ko 1-4 the highest concentration of THMs was approx. 50 µg/L which was detected in Ko 2 and was significantly lower in the other three samples. For ML 1 and ML 2, THM concentrations of approx. 100 µg/L and 240 µg/L were measured. A possible explanation is the different work-up of the filling water. In Ko 1-4 the cooling water was regained by condensation. At this step, at least some of the THMs could volatilise. In ML 1 and 2, reverse osmosis was used for work-up of the water. This example of the cooling systems Ko 1-4 and ML 1, 2 demonstrated another factor, not directly related to the disinfection process, that may have influenced the DBP concentrations after a disinfection. In the ML 2 sample, a very high concentration of >2000 µg/L acetaldehyde was detected. As the sample was remeasured delivering similar results, a possible contamination could only have occurred already at sampling time. But the result was not

necessarily caused by a contamination. The matrix loading in ML 1 and 2 was stated to be generally low but situationally high by corrosion products and glycol. Such situational high matrix loading may be responsible for the acetaldehyde results.

6.7 Preliminary conclusions

The analytical results presented in this chapter clearly show the complex system of reactions taking place after applying a.s. in presence of matrix and water. These reactions do not only consist of reactions of the a.s. with organic and inorganic matrix constituents but include continuous reactions between the a.s., matrix and already formed DBPs. The factors influencing this reaction system evaluated during this project were a.s. concentration, water availability, TOC concentration, TOC contents, temperature, time and pH. While the goal of the project initially was to identify the worst-case conditions for the formation of DBPs to derive formation fractions used in exposure assessment, it became clear that the system is too interconnected to define such a worst-case, even in controlled laboratory conditions. Conditions leading to a high formation of a specific class of DBPs might at the same time lead to a deceased formation of another class. A mere increase of the same matrix can not only change the amount of DBPs produced but also their composition. The genuine samples from real disinfection processes underline this finding. In reality, even more factors such as technical operations during water processing or other chemicals added to the water will influence the formation of DBPs.

Within this project, we were not able to understand all processes influencing the DBP formation. The partially unexpected results indicate that unknown parameters with an influence on DBP formation might not have been controlled in the experiments. This is further supported by the results of the experiments on reproducibility, that showed the reproduction unfortunately is only limited, even when conducted by the same laboratory. Furthermore, the project was limited to target analyses and thus to a reduced set of DBPs. Especially for non-halogenating a.s. such as hydrogen peroxide this limits the findings of the project. Non-target analyses of the samples might improve the future understanding of the processes but was not covered in the project.

The results show that despite extensive experimental work, the project was not able to produce values that could be used as formation fraction for the calculation of PECs for DBPs that would be needed for a single substance assessment of DBPs. This needs to be taken into account when developing an approach for the environmental risk assessment considering DBPs.

7 Conclusions for environmental risk assessment of DBP

7.1 ECHA Guidance on Disinfection By-Products

The ECHA Guidance on Disinfection By-Products (ECHA, 2017) provides a general approach for the environmental risk assessment of DBPs. However, it only considers halogenated DBPs, consequently the relevant group of non-halogenated DBPs is not considered. In addition, it is only focussing on the biocidal product types (PT) 2 (disinfectants and algaecides, not intended for direct application to human or animals), 11 (preservatives for liquid-cooling and processing systems) and 12 (slimicides). Other PTs for which a DBP-assessment may be needed are PT 1, 3, 4 and 5. In the conclusions of the guidance, it is recommended to further investigate its applicability to these PTs.

The textbox provides a summary of the guidances approach taken from its conclusion.

Textbox – Citation of the conclusion of Guidance on Disinfection By-Products (ECHA, 2017)

"This document provides a scientifically based strategy for the environmental risk assessment of disinfection by-products (DBPs) in the context of biocides authorisation under European legislation. The risk assessment of DBPs follows the scenarios applied for the active substance and should include all relevant compartments.

The risk assessment includes three steps which should be used, as required, to underpin the absence of unacceptable effects.

- an initial worst-case risk assessment for a set of known marker DBPs, using a PEC/PNEC approach assuming 100% conversion of the biocidal active substance;
- chemical assessments in which (changes in) group parameters (e.g. AOX; adsorbable organic halogens) are determined;
- a refined risk assessment for known marker DBPs, appended with a whole effluent testing (WET)-approach to cover unknown DBPs.

The known DBP-groups that should at least be included in the risk assessment are: trihalomethanes (THMs), halogenated acetic acids (HAAs), halogenated acetonitriles (HANs), bromate, halogenated phenols, and halogenated amines. In principle all individual compounds of the DBP-groups should be addressed in the risk assessment. Specific compounds may be excluded based on argumentation, additional DBPs should be included if there are indications from e.g. measurements or theoretical considerations that a particular biocidal use leads to their formation.

Exposure of DBPs may be estimated by modelling, actual measurements, or by a combination of both. Simulation studies can be used to derive realistic worst-case formation percentages. [...]"

Discussion of the guidance based on our findings

The ECHA guidance describes correctly the potential complexity when dealing with DBPs, pointing out that hundreds of DBPs are already mentioned in the literature and that sum parameters (e.g. AOX) indicate that despite the high number, still approx. 50% even of the halogenated DBPs are not identified.

Although the literature search on DBPs (chapter 2) has significant limitations as described in section 2.3.5 arising from the focus on chlorinating a.s. in the literature studies, still a significant number of **non-halogenated DBPs** was identified. These DBPs are not considered in the current guidance, which needs to be amended. For a comprehensive overview on relevant DBPs, an

additional focus needs to be put on non-halogenating but highly reactive biocidal a.s. like peroxides or ozone. For those substances, there would be further need for experimental studies as only very limited information is available in the existing literature. It appears possible that important DBPs generated during use of non-halogenating but highly reactive biocidal a.s. are still not identified.

For uses in **non-aqueous systems** (e.g. hard surfaces, when the only water source is the a.s. formulation) another data lack was identified in our literature search. No literature data was found referring to disinfection uses in non-aqueous systems and no test guidelines are available for these uses. As the absence of water can influence chemical reactivity and reactions, also generation of DBPs can be different as shown in chapter 6. Again, it may well be that main DBPs are not identified yet and thus not sufficiently considered in the existing guidance.

A three step approach has been recommended in the ECHA guidance, which is still challenging:

For the **first step**, suitable PNEC values for all known marker DBPs and for different compartments are a prerequisite. This may be based on QSAR or read across, but experimental studies shall be preferred. Group ecotoxicity assessment may decrease the workload, but needs, as already discussed in the guidance, a justification (weight-of-evidence) based on data for the individual compounds.

From our point of view, it is reasonable to select marker DBPs as general indicators for the generation of DBPs to potentially reduce the effort needed. Within an environmental risk assessment, the identification of a marker DBP could be a trigger for more detailed analyses. However, for each of these marker DBPs also an own exposure assessment is necessary, which needs additional information such as fate and behaviour in the environment ((bio)degradation, partitioning, etc). The inherent information about the marker DBPs can be shared between the stakeholders, still requiring a dossier for all known marker DBPs which has to be coordinated between authorities and interesting industry parties. And while inherent properties of the marker DBP remain the same over different dossiers, use conditions may be different for each biocidal dossier and use, and thus immense effort on exposure assessment is necessary already for this first step. The value of information gained by this already extensive work load is, however, limited as usually 100% conversion of a.s. to DBP is assumed, leading to very conservative assessments.

For the **second step**, group parameters (e.g. AOX) are used to evaluate the potential changes in the toxic potential through DBP formation. However, the knowledge about the connection between changes in the group parameters and the toxicity is limited. If different DBPs will be formed, the effect may be different, and thus without increasing knowledge about the single DBPs and their formation potential, this approach may be of limited gain of information for the environmental risk assessment.

Finally, there would be still some uncertainties following step 1 and 2 with regard to unknown DBPs, so that often whole effluent testing (WET) or tailor-made studies would be required (**step 3**). An advantage by using the group parameters and/or the WET is that mixture toxicity is potentially considered, especially if similar DBPs are formed with similar mode of action (additive toxicity) regardless if the specific DBPs are known or unknown. However, **WET** is limited to aqueous systems and delivers only a sum parameter. Regarding the experiments performed within the present study it is questionable if this can be done in a sufficiently reproducible way (see section 6).

The same applies to **tailor made studies** for marker DBP, for example to derive a refined formation fraction. The experiences within this study concerning simulation testing and analyses of real samples show a high uncertainty with view on an appropriate feasible approach.

Detailed recommendations and guidelines for such measurements would be essential for each biocidal use. To be able to give those recommendations, further knowledge and fundamental research would be needed, which is not expected to be conducted in foreseeable time. The formation of DBPs is a complex system of reactions taking place after applying biocidal a.s. in presence of matrix and water. This complex system may vary between product types or even within product types in different settings. In addition, the experiences show that simulation testing will be not able to (re)produce values that could be used to derive a formation fraction for the calculation of PECs for DBPs that would be needed for a refined single substance assessment of DBPs. As explained above, it remains unclear how to conduct these detailed analyses based on the complexity of the issue and many parameters influencing the reactions. New findings regarding DBP formation might change this conclusion but this is not expected in the forseeable future. This lack of a feasible approach to conduct simulation experiments or to derive a formation fraction leads to the situation that only known DBPs can be assessed in most cases. In specific cases, specific formation fractions due to experimental results may be justified in a weight of evidence approach and considered within the environmental risk assessment of the DBPs. This is for example the case if for specific uses and conditions several monitoring data or simulation tests are available which are regarded as sufficiently reliable for this specific use.

Considering this, it is doubtful, if the experimental testing proposed in the ECHA guidance will be able to deliver the necessary information on the generated DBPs or, to be more precise, if the design of such studies with a reasonable effort is possible. Moreover, not for all uses and a.s. combinations, WET testing is possible at all.

Overall, the approach described in the current ECHA guidance is challenging, and needs a lot of effort by authorities and industry parties. Moreover, the three step approach described in the guidance will only cover some of those uncertainties with regard to DBP formation. Despite all efforts, the results might still not be sufficient to ensure that DBPs have been considered in an adequate way for all active substances. Furthermore, due to the generic character of the existing guidance and the lack of detailed instructions and requirements, a consistent interpretation by all competent authorities is questionable. As a consequence, a harmonized scientific based environmental risk assessment of DBPs is currently not conducted and an easy way for mutual recognition of product approval is not guaranteed.

7.2 Discussion of improvements for DBP environmental risk assessment

This chapter presents potential aspects, approaches and concepts for an improvement of the environmental risk assessment of DBPs. However, based on the results within this project, further development of the environmental risk assessment of DBPs is challenging. As described above, the gain of information based on group parameters is very limited. Furthermore, it seems questionable whether meaningful simulation studies for a refined risk assessment are possible with reasonable effort. Also WET is only possible in aqueous systems, so refinement options seem to lack completely for non-aqueous systems.

For this reason, the conclusions of this project how to improve environmental risk assessment of DBPs focus on discussion of aspects which may be considered to further develop and harmonise the initial risk assessment of DBPs.

7.2.1 Definition of DBPs

Definition of DBPs has been given within this project in chapter 2.1. This definition differentiates between transformation products (TP) which will be formed in the environment and the DBP which will be formed during application (use). In addition, DBP and TP should be differentiated

to impurities (or other ingredients) in the biocidal product as well as reaction by-products of in-situ substances, e.g. by hydrolysis.

Textbox – Definition of DBPs

DBPs are defined as reaction products of the biocidal active substance with the matrix present during the application of the biocidal product.

7.2.2 Criteria to rule out DBP formation

Within this project, the likeliness of DBP formation has been assessed for the active substances based on literature search and expert judgements. The likeliness refers to the capability of DBP formation, not to the degree of DBP formation. Furthermore, this terminology is not related to possible effect concentrations. For risk assessment purposes, 'unlikely' can be interpreted as DBP formation is not expected but cannot be fully excluded. 'Likely' can be interpreted as DBP formation is certain as verified in literature or at least more probable than no DBP formation. It seems to be reasonable that only for those active substances that have been judged as "likely" to form DBP a consideration of the DBP environmental risk assessment is potentially necessary.

The literature review showed for which active substances DBPs have already been identified. Usually these are oxidising substances and/or halogenating substances. In addition, several other structural information indicate for which substances DBP formation is most likely. Based on this exercise criteria can be established to rate the substances as "unlikely". The criteria may be adapted, if further information about DBP formation is available.

Textbox – Criteria to rule out DBP formation

Environmental risk assessment for potential DBP need not to be conducted, i.e. DBP formation is "unlikely", if:

Substance is
not classified as oxidising gas, liquid or solid (H270, 271, 272) or
not classified as organic peroxides (H240, 241 und 242)

and

1. Organic substances:
   (a) does not contain triple bonds or radicals
   (b) does not contain oxygen, chlorine, bromine, iodine
   (c) if contains chlorine, bromine or iodine, these are forming only
      - separate monoatomic ions (counterions) or
      - single bonds to a carbon atom
   (d) if contains oxygen, these are forming only
      - separate ions (counterions (SO_4^{2-} or OH^-)) or
      - single bonds to carbon or hydrogen or
      - a carboxylate moiety

2. Inorganic substances:

   (a) does not contain oxygen, chlorine, bromine, iodine

   (b) if contains oxygen, chlorine, bromine or iodine, these are only as monoatomic ions (halides) or hydroxide ion, phosphate or sulfate ion (oxygen)

These screening criteria indicate for which active substances DBP formation is not expected. Within the project, all other active substances that do not fulfil these criteria, were rated "likely". However, not for all of these compounds specific DBPs have been identified so far. It is still possible that some of these compounds do not form DBP, i.e. are false positive. For this reason, future research and knowledge is needed to reduce the number of false positives. This research should result in requirements and conditions for an appropriate (analytical) procedure for identification of DBPs (simulation testing or monitoring studies). Without this specific guidance, it has to be discussed whether, and if so how, all of these (unknown) substances should be considered for DBP environmental risk assessment or only the substances where DBP formation is definitely known.

7.2.3 Categories of active substances and their potential DBPs

Within the project, the already identified DBPs have been assigned to specific categories of active substances based on the chemical structures of the active substances. See chapter 4 for explanation why it was not possible to assign DBPs to specific active substances but only to categories.

If DBPs are assessed in a single substance approach, the tables and categorisation provided in chapters 2 and 3 would help to identify the already known potential DPBs for each active substance. This means that if a biocidal active substance can be assigned to a specific category, the DBPs mentioned for this category would have to be evaluated if relevant for this biocidal active substance under the given use conditions. For example, if a biocidal active substance contains a peroxide group, it can be assigned to category 2.2, and the potential DBPs given for the category 2.2 would have to be evaluated in the assessment of this biocidal active substance.

In addition, the categories could be used for a starting point for grouping the DBPs within each category, and to select marker DBPs per sub-group of DBPs covering all other DBPs in this category. Probably the approach to decide on similar mode of entry and distribution given in chapter 3 combined with effect data may be useful to decide on such sub-groups. For these marker DBPs, preparation and organization of shared dossier preparation would be advisable.

7.2.4 Relevance of DBPs for individual environmental risk assessment

Using the information given above (definition, likeliness, categories), several DBPs have been assigned to groups of active substances. However, not all of these potential DBPs are relevant for each biocidal active substance of this group under specific use conditions, and thus potentially not for each of these DBPs an individual environmental risk assessment is required.

The results of the project show that there is often not enough data to exclude specific DPBs based on the use conditions. One single example where DBPs might be excluded due to use conditions are chlorinations conducted in water not containing any iodine or bromine. In this case, any iodine or bromine containing DBPs might be excluded.

In the following, further aspects will be discussed to further reduce the number of potential DBPs under investigation.

Relevance of substances such as impurities, by-products, or metabolites have already been discussed in the respective chapter of the BPR guidance. It is important to note that a harmonization of the requirements is favoured. According to the BPR guidance "*Ecotoxicologically relevant metabolite are metabolites which poses a higher or comparable hazard to any organism as the active substance. In general, an environmental risk assessment for the relevant compartments need to be performed for all ecotoxicologigally relevant metabolites (minor and major)*" (ECHA 2017).

In accordance with the definition of relevance for metabolites, ecotoxicologically **relevant DBPs** would be DBPs which pose a higher or comparable hazard to any organism as the active substance. For this reason, the relevance of a DBP is influenced by the expected **ecotoxicological** as well as **fate and behaviour properties** of the DBP in comparison to the active substance.

Ecotoxicity of DBPs

Developing an approach how to consider ecotoxicological potential of DBPs in the evaluation process was not part of the project. However, an approach to consider different ecotoxicological potential in comparison to the active substance could be the DBP factor (see below).

Fate and behaviour of DBPs

For the fate, two different properties have been discussed within the project.

First, some DBPs may be very reactive, and will react within seconds or minutes to follow-up products. In this case, the life-time of the DBP in the environment is expected to be too short to induce significant effects. For this reason, DBPs may not be relevant if the DBP is very short-lived. As discussed in chapter 5.2, a relevant trigger for short-lived DBPs may be < 6 h.

The second property is based on the route of entry into the environment, i.e. the distribution of the DBP during or after application (use). The environmental risk assessment of the biocidal a.s. is only adequate for the DBP if the distribution of the DBP is similar to the biocidal a.s.. If the route of entry into the environment is different between the DBP and the biocidal a.s., the risk assessment of the biocidal active substance maybe only of limited value for the DBP, and thus not reliable. If this is the case, an individual risk assessment may be necessary.

Within the project, an approach has been proposed on how to evaluate the comparability of DBPs with a.s. (chapter 5.2). A trigger value of 10% was used as a first attempt to identify different behaviour leading to the requirement of a single substance assessment of the respective DBP. As equilibrium conditions are presumed, the evaluation has some uncertainties, and this is reflected in the trigger. Two different exemplary "scenarios" covering aqueous solution and surface treatment have been presented to estimate if DBPs behave similar or different compared to the biocidal a.s. (chapter 5.3).

Environmental risk assessment of DBPs

For the consideration of relevant DBP in environmental risk assessment, there are two cases:

A DBP may be relevant for the environment based on above definition but all effects might already be covered within the risk assessment of the active substance if it is comparable in its fate and effects. This might be the case if its ecotoxicity is equal to that of the a.s. and its fate and behaviour is comparable. This has the consequence, that no single substance assessment of this DBP would be necessary.

In the second case, DBPs are considered as relevant but because of their higher ecotoxicity or their different fate and behaviour their risk is not already covered by the assessment of the active substances. For these DBP, individual risk assessment is necessary.

7.2.5 Pragmatic approach using a DBP factor in a first step

To reduce the effort needed for an environmental risk assessment of DBP, a more generic approach using a DBP factor as a first step might be promising. In such an approach the existing risk assessment (RCR = PEC/PNEC) for the active substance, which in any case has to be performed, may be used also for the DBPs.

The uncertainty with regard to the ecotoxic potential of the known and unknown DBPs in comparison to the active substance should be covered by a generic DBP factor, which can be applied to the PNEC value of the active substance. For the derivation of such a DBP factor, the ecotoxic potential of presently known DBPs should be compared to their active substance. Probably the 75th percentile of all these ratios can be used as a generic DBP factor covering all known and unknown DBPs.

If the PEC/PNEC values of the active substance are used also for the DBPs, the PEC values have to be converted to the molar formation of the DBPs considering the degree of formation (100% as a worst-case). However, if fate and behaviour of the DBP is significantly different in comparison to the active substance, the PEC/PNEC value of the a.s. potentially will not cover the DBPs sufficiently. For example, for hydrogen peroxide usually a fast degradation in sewage treatment plants has been considered in the risk assessment. If the DBPs evaporate and thus will not be emitted down-the drain or are not degraded in such a fast rate, the PEC for the active substance cannot be used as surrogate for the PEC of the DBPs. Depending on the compartment, an overestimation and underestimation of the risk is possible. For this reason, the DBP factor approach should actually only be applied to cover those DBP with a similar fate and behaviour. DBPs not fulfilling those criteria would still need single substance assessment. An alternative will be to consider this uncertainty also in the generic DBP factor, and not only the different ecotoxicity, especially if the difference in fate is expected to be of minor impact. It has to be clarified if and in which cases a DBP factor approach can cover this uncertainty in the fate and behaviour.

If both factors are considered multiplicative, a DBP factor covering all uncertanties with regard to potential unknown or known DBPs is potentially very high. This would result in single substance assessments being needed for most of the DBPs anyway and would thus not reduce the workload. For example, assuming that the ecotoxic potential of an unknown DBP might be up to a factor of 10 higher, and the PEC increases by a factor of 10, an appropriate overall DBP factor would be 100. This would probably often result in unacceptable risk for DBP forming active substances. Also, it has to be taken into account how many uncertainties the assessment factor of 10 for PNEC derivation still covers, and a DBP factor conserably lower than this might also be thinkable. In this context, also the TTC approach (Threshold of Toxicological Concern, Gutsell et al., 2015; Hennes, 2012; Gross et al., 2010) may be helpful or approaches such as at which level negligible exposure is expected.

Overall, if such a DBP factor was possible this would decrease significantly the effort necessary for the assessment of individual DBPs for each biocidal use. The implementation of a DBP factor approach into DBP evaluation may be challenging but if the factors are balanced between the need on decreasing uncertainty of the unknown effects by unknown DBPs and the increase of the protection of the environment, this may result in an improvement and in a consistent and easier evaluation of DBPs in comparison to the existing guidance.

7.3 Conclusion

One objective of the project was to find ways to generate meaningful results for the environmental risk assessment of DBPs while at the same time keep the effort of DBP evaluation manageable. For this reason, the project concluded that the results presented and discussed above can be used to propose a way forward in further developing the environmental risk assessment of DBPs. Following aspects and approaches may be considered:

- Definition of DBPs

- Criteria to rule out DBP formation
- Categories of active substances and their potential DBPs
- Relevance of DBPs for individual environmental risk assessment
- DBP factor approach in a first step

Different approaches would be needed for known and unknown DBPs. Only for specific cases of already known DBPs, a single substance DBP environmental risk assessment is possible and should be applied. Others should be covered by including a DBP factor as a first step. For known DBPs, analyses of group parameters, refinements by simulation testing or analysis of real samples seem not to be able to generate further results that would contribute to a better environmental risk assessment. However, in specific cases a weight of evidence on formation fractions based on experimental results may be justified and considered within the environmental risk assessment of the DBPs.

However, especially for so far unknown DBPs, an adequate assessment is still challenging. It has to be clarified if a DBP factor approach can cover the uncertainty by these unknown substances. If unknown DBPs are expected, simulation testing using non-target analyses may be required to identify DBPs. If possible, whole effluent testing should support these analyses to generate knowledge of potential effects due to unknown DPBs. However, in this case better understanding and guidance for harmonized and standardaized conditions of such simulation testing and effluent testing is still needed.

Research needs have been identified: (a) to analyse appropriate DBP factors for the difference in the ecotoxic potential and in the expected exposure concentrations between a.s. and DBPs. (b) Adequate trigger values for difference in mode of entry/distribution should be discussed. (c) Further development of simulation testing (guidelines) are desirable for different PT or even subgroups (applications). Without a better standardisation, harmonization and validation of such a simulation testing, the results are not reliable for environmental risk assessment due to the expected high variability.

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9 Annex

A List of DBPs identified in literature

Table 21: Overview of halogenated DBPs found in the literature search

DBP	CAS
Trihalomethanes (THM)	
trichloromethane	67-66-3
bromodichloromethane	75-27-4
dibromochlormethane	124-48-1
tribromomethane / bromoform	75-25-2
dichloroiodomethane	594-04-7
bromochloroiodomethane	34970-00-8
dibromoiodomethane	593-94-2
triiodomethane / iodoform	75-47-8
chlorodiiodomethane	593-71-5
iodomethane	74-88-4
chloroiodomethane	593-71-5
diiodomethane	75-11-6
bromodiiodomethane	557-95-9
Other Haloalkanes	
hexachloroethane	67-72-1
iodoethene	593-66-8
Haloacetic acids (HAAs)	
dichloroacetic acid	79-43-6
trichloroacetic acid	76-03-9
bromochloroacetic acid	5589-96-8
dibromoacetic acid	631-64-1
bromodichloroacetic acid	71133-14-7
dibromochloroacetic acid	5278-95-5
chloroacetic acid	79-11-8
bromoacetic acid	79-08-3
tribromoacetic acid	75-96-7
iodoacetic acid	64-69-7
diiodoacetic acid	598-89-0
triiodoacetic acid	594-68-3
Other Haloacids	
2,4-dichlorophenylacetic acid	19719-28-9
2,2-dichloropropanoic acid	75-99-0
3,3-dichloropropenoic acid	1561-20-2
cis-2,3-bromochloropropenoic acid	1561-20-2
trans-2,3-bromochloropropenoic acid	1561-20-2
2,3-dibromopropanoic acid	600-05-5
cis-2,3-dibromopropenoic acid	600-05-5
trichloropropenoic acid	2257-35-4
2-bromo-3,3-dichloropropenoic acid	2257-35-4
3-bromo-2,3-dichloropropenoic acid	2257-35-4
2-chloro-3-methylbutanoic acid	921-08-4

DBP	CAS
tribromopropenoic acid	71815-46-8
2-chloro-2-methylpropanoic acid	594-58-1
Halodiacids	
cis-bromobutenedioic acid	584-99-6
trans-bromobutenedioic acid	644-80-4
cis-bromochlorobutenedioic acid	644-80-4
trans-bromochlorobutenedioic acid	644-80-4
cis-dibromobutenedioic acid	644-80-4
(E)-2-chloro-3-methylbutenedioic acid	644-80-4
2-chlorobutenedioic acid	617-42-5
(R*,S*)-2,3-dichlorobutanedioic acid	3856-38-9
2,2-dichlorobutanedioic acid	3856-37-9
Haloacetonitriles (HANs)	
dichloroacetonitrile	3018-12-0
trichloroacetonitrile	545-06-2
bromochloroacetonitrile	83463-62-1
dibromoacetonitrile	3252-43-5
chloroacetonitrile	107-14-2
bromoacetonitrile	590-17-0
dibromochloroacetonitrile	144772-39-4
iodoacetonitrile	624-75-9
Haloacetamides (HAcAms)	
2,2-dichloroacetamide	683-72-7
2,2-dibromoacetamide	598-70-9
2,2,2-trichloroacetamide	594-65-0
bromochloroacetamide	62872-34-8
bromodichloroacetamide	98137-00-9
dibromochloroacetamide	855878-13-6
tribromoacetamide	594-47-8
chloroiodoacetamide	62872-35-9
bromoiodoacetamide	62872-36-0
diiodoacetamide	5875-23-0
2-chloroacetamide	79-07-2
2-bromoacetamide	683-57-8
iodoacetamide	144-48-9
Halonitromethanes (HNMs)	
chloronitromethane	1794-84-9
bromonitromethane	563-70-2
dichloronitromethane	7119-89-3
bromochloronitromethane	135531-25-8
dibromonitromethane	598-91-4
trichloronitromethane / chloropicrin	76-06-2
dibromochloronitromethane	1184-89-0
tribromonitromethane	464-10-8
Haloketones (HKs)	

DBP	CAS
1,1,1-trichloro-2-propanone	918-00-3
1-chloropropanone	78-95-5
chloropropanone	78-95-5
1,1,3-trichloropropanone	921-03-9
1,1-dichloropropanone	513-88-2
bromopropanone	598-31-2
1-bromo-1-chloropropanone	34652-54-5
1,1-dibromopropanone	867-54-9
1,1,3,3-tetrachloropropanone	632-21-3
1,3-dichloropropanone	534-07-6
1,1,1-trichloropropanone	918-00-3
4,4-dibromobutan-2-one	785803-12-5
1,1,1,3,3-pentachloropropanone	1768-31-6
Haloaldehydes	
chloroacetaldehyde	107-20-0
bromoacetaldehyde	17157-48-1
iodoacetaldehyde	55782-51-9
dichloroacetaldehyde	79-02-7
bromochloroacetaldehyde	98136-99-3
dibromoacetaldehyde	3039-13-2
trichloroacetaldehyde	75-87-6
bromodichloroacetaldehyde	34619-29-9
dibromochloroacetaldehyde	64316-11-6
tribromoacetaldehyde	115-17-3
Haloamines	
trichloramine	10025-85-1
monochloramine	10599-90-3
dichloramine	3400-09-7
Dichloromethylamine	7651-91-4
Halobenzoquinones	
2,6-dichloro-1,4-benzoquinone	697-91-6
2,6-dichloro-3-methyl-1,4-benzoquinone	-
2,3,6-trichloro-1,4-benzoquinone	634-85-5
2,6-dibromo-1,4-benzoquinone	19643-45-9
2,3-dibromo-5,6-dimethyl-1,4-benzoquinone	38969-08-3
2,3,5,6-tetrabromo-1,4-benzoquinone	488-48-2
Other	
chloral hydrate	302-17-0
bromal hydrate	507-42-6
cyanogen chloride	506-77-4
cyanic bromide	506-68-3
benzyl chloride	100-44-7
α,α-dichloroacetophenone	2648-61-5
2-chloro-acetophenone	532-27-4
6-chloro-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine	6190-65-4

DBP	CAS
4-bromo-2-chlorophenol	3964-56-5
2,4,6-trichlorobenzonitrile	6575-05-9
N-(4-bromo-2-chlorophenyl)-acetamide	3460-23-9
4-bromo-3-chloroacetanilide	22459-81-0
2-chloro-ethanesulfonyl chloride	1622-32-8
chloromethanesulfonyl chloride	3518-65-8
1-bromo-3-chloro-2-methyl-benzene	62356-27-8
1,4-Dichlorobenzene	106-46-7
2-chlorophenylacetonitrile	2856-63-5
3,4-dichlorophenylacetonitrile	3218-49-3
3-chlorotyrosine	7423-93-0
dichloromethyl methyl sulfone	37557-96-3
4-monochlorophenol	106-48-9
2,4-dichlorophenol	120-83-2
2-bromophenol	95-56-7
4-bromophenol	106-41-2
2-amino-4-bromo-phenol	40925-68-6
2,6-dichloro-4-nitrophenol	618-80-4
2,4-dibromophenol	615-58-7
2,6-dibromophenol	608-33-3
2-bromo-6-chloro-4-nitrophenol	619-08-9
2,6-dibromo-4-methyl-phenol	2432-14-6
4-amino-2,6-dibromo-phenol	609-21-2
2,6-dibromo-5-nitrophenol/(2,6-Dibromo-4-nitrophenol)	99-28-5
Monobrominated Avobenzon	-
Dibrominated Avobenzon	-
Monobrominated OMC	-
Dibrominated octylmethoxy cinnamate	-
Dibrominated Dioxybenzone	-
Tribrominated Dioxybenzone	-
Tetrabrominated Dioxybenzone	-
Ethyl iodoacetate	623-48-3
3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone	77439-76-0
Dibromoacetonitrice	3252-43-5
3-Acetyl-dihydro-2(3H)-furanone / 2-Acetylbutyrolactone	517-23-7
3-Chloro-methyl paraben	3964-57-6
3,5-dichloromethyl paraben	3337-59-5
3-Chloro-ethyl paraben	16357-41-8
3,5-dichloroethyl paraben	17302-82-8
4-Bromotoluene	106-38-7
Inorganic ions	
Bromate	15541-45-4
Bromide	24959-67-9
Chlorate	14866-68-3
Chlorite	14998-27-7

DBP	CAS
Halogenated fatty amides	
Hydroxychlorooctadecanamide (both isomers)	-
Dichlorooctadecanamide (both isomers)	-
Hydroxybromooctadecanamide (both isomers)	-
Hydroxychlorodocosanamide (both isomers)	-
Hydroxybromodocosanamide (both isomers)	-
Hydroxychlorohexadecanamide (both isomers)	-
Dichlorohexadecanamide (both isomers)	-
Dihalo-4-hydroxybenzaldehydes	
3,5-dichloro-4-hydroxybenzaldehyde	2314-36-5
3-bromo-5-chloro-4-hydroxybenzaldehyde	1849-76-9
2,6-dibromo-4-hydroxybenzaldehyde	856767-00-5
Dihalo-4-hydroxybenzoic acids	
3,5-dichloro-4-hydroxybenzoic acid	3336-41-2
3-bromo-5-chloro-4-hydroxybenzoic acid	118276-15-6
3,5-dibromo-4-hydroxybenzoic acid	3337-62-0
Dihalo-salicylic acids	
3,5-dichlorosalicylic acid	320-72-9
3-bromo-5-chlorosalicylic acid	4068-58-0
3,5-dibromosalicylic acid	3147-55-5
Trihalo-phenols	
2,4,6-trichlorophenol	88-06-2
2,6,-dichloro-4-bromophenol	88-06-2
2,6-dibromo-4-chlorophenol	5324-13-0
tribromophenol	118-79-6
3,4,5-tribromo-2-methoxyphenol	113800-64-9
2,3,5-Tribromo-1H-Pyrrole	69624-12-0

Table 22: Overview of non-halogenated DBPs found in the literature search

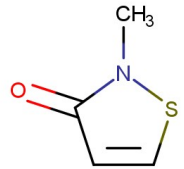
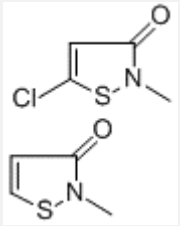
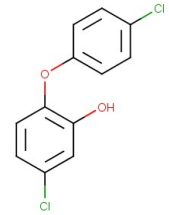
DBP	CAS
Nitrosamines (NA)	
N-nitrosodimethylamine	62-75-9
N-nitrosomorpholine	59-89-2
N-nitrosodiethylamine	55-18-5
N-nitrosopiperidine	100-75-4
nitrosodibutylamine	924-16-3
N-nitrosopyrrolidine	930-55-2
N-nitrosomethylamine	64768-29-2
N-nitrosodi-n-propylamine (NDPA)	621-64-7
N-nitrosoethylmethylamine (NEMA)	10595-95-6
N-nitrosodiphenylamine	86-30-6
Other	
3-methyl-2-pentyl-2-cyclopenten-1-one / dihydrojasmone	1128-08-1
3-hepten-2-one	1119-44-4
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22.2

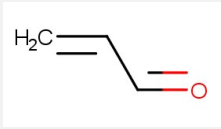
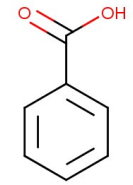
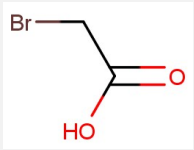
DBP	CAS
acetophenone	98-86-2
1(3H)-isobenzofuranone	87-41-2
phthalic anhydride	85-44-9
9,10-anthracenedione	84-65-1
tributyl citrate	77-94-1
4-ethoxy-benzoic acid ethyl ester	23676-09-7
dodecyl acrylate	2156-97-0
hexahydro-1-methyl-2H-azepin-2-one	2556-73-2
N-cyclohexyl-2-pyrrolidone	6837-24-7
δ-nonalactone	3301-94-8
dibenzofuran	132-64-9
1-methyl-2,5-pyrrolidinedione	1121-07-9
1-methyl-2-pyrrolidinone	872-50-4
N-acetylpyrrolidone	932-17-2
phthalimide	85-41-6
α,α-dimethyl-benzenemethanol	617-94-7
2-butoxy-ethanol	617-94-7
benzaldehyde	100-52-7
(E)-2-nonenal	18829-56-6
4-ethyl-benzaldehyde	4748-78-1
4-methoxy-benzaldehyde	123-11-5
2,2'-azobis(2-methylpropanenitrile)	78-67-1
styrene	100-42-5
1-ethyl-2,4-dimethyl-benzene	874-41-9
1-methyl-naphthalene	90-12-0
2,5-bis(1,1-dimethylethyl)-4-ethyl-phenol	4130-42-1
1,2,4-trimethylbenzene	95-63-6
1-methoxy-4-methylbenzene	104-93-8
benzoic acid methyl ester	93-58-3
phthalic acid	88-99-3
diethyl phthalate	84-66-2
benzophenone	119-61-9
nitrate	14797-55-8
formaldehyde	50-00-0
acetaldehyde	75-07-0
n-propanal	123-38-6
n-pentanal	110-62-3
cyclohexanone	108-94-1
n-hexanal	66-25-1
heptanal	111-71-7
octanal	124-13-0
n-nonanal	124-19-6
decanal	112-31-2
glyoxal	107-22-2
methyl glyoxal	78-98-8

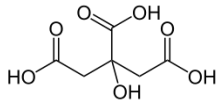
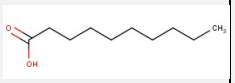
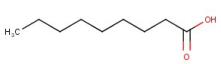
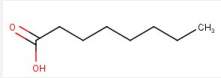
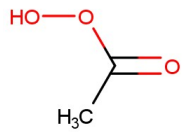
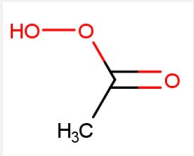
DBP	CAS
cyanuric acid	108-80-5
N-morpholine	109-02-4
N-methyl-2-pyrrolidone	872-50-4
N-Cl-tyrosylglycine	2095513-62-3
N,N-di-Cl-tyrosylglycine	2095513-63-4
N-Cl-phenylalanylglycine	201216-27-5
N,N-di-Cl-phenylalanylglycine	2095513-64-5
N-Cl-tyrosylalanine	2095513-65-6
N,N-di-Cl-tyrosylalanine	2095513-66-7
2-furancarboxaldehyde	98-01-1
5-methyl-2-furancarboxaldehyde	620-02-0
Carboxylic acids	
butyric acid	107-92-6
decanoic acid	334-48-5
dodecanoic acid	143-07-7
butyl acetate	123-86-4
glycolic acid	79-14-1
hexanoic acid	142-62-1
2-methylbutyric acid (RIS)	116-53-0
oleic acid	112-80-1
oxalic acid	144-62-7 (anhydrous)
propionic acid	79-09-4
pyruvic acid	127-17-3
benzoic acid	65-85-0
3-hydroxybenzoic acid	99-06-9
2-nitrobenzoic acid	552-16-9
phenylacetic acid	103-82-2
salicylic acid	69-72-7
m-toluic acid	99-04-7
o-toluic acid	118-90-1
p-toluic acid	99-94-5
acetic acid	64-19-7
decanoic acid	334-48-5
1,2,3-Benzenetricarboxylic acid	732304-21-1
4-nitrobenzoic acid	62-23-7
phthalic acid	88-99-3
glyoxylic acid	298-12-4

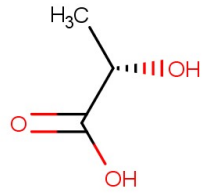
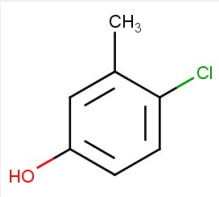
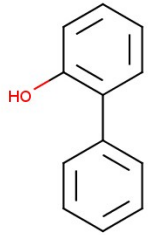
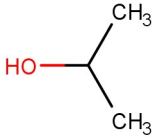
B Evaluation of biocidal active substances reading their DBP formation potential

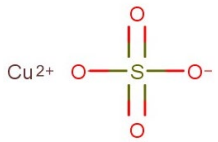
Table 23: Evaluation of biocidal active substances reading their DBP formation potential

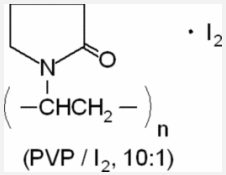
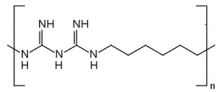
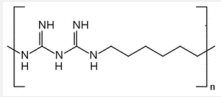
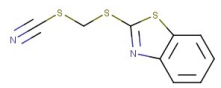
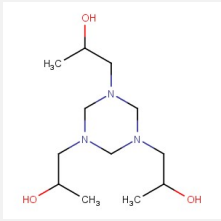
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
2-Methyl-2H-isothiazole-3-one (MIT)	1	2682-20-4	11, 12	C4H5NOS		systemic [isothiazolone]	2.7	unlikely	no
5-Chloro-2-methyl-3(2H)-isothiazolone with 2-methyl-3(2H)-isothiazolone (mixture) (CMIT)	1	55965-84-9	2, 4, 11, 12	C4H5NOS. C4H4ClNOS		systemic [isothiazolone]	2.7	unlikely	no
5-Chloro-2-(4-chlorophenoxy)phenol (DCPP)	1	3380-30-1	1, 2, 4	C12H8Cl2O2		systemic	2.4	unlikely	no

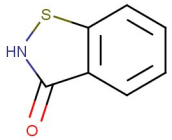
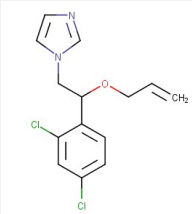
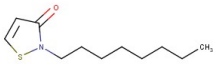
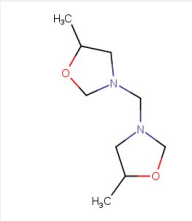
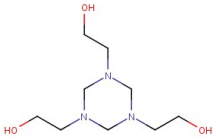
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Acrolein	1	107-02-8	12	C3H4O		active carbonyl	2.3.1	likely	no
Active chlorine released from calcium hypochlorite	1	7778-54-3	2, 3, 4, 5	CaCl2O2		halogene [chlorination]	1.1.2	likely	yes
Active chlorine released from chlorine	1	7782-50-5	2, 5	Cl2		halogene [chlorination]	1.1.3	likely	yes
Active chlorine release from sodium hypochlorite	1	7681-52-9	1, 2, 3, 4, 5	ClNaO		halogene [chlorination]	1.1.2	likely	yes
Amines, N-C10-16-alkyltrimethylenedi-, reaction products with chloroacetic acid (Ampholyt 20)	1	139734-65-9	2, 3, 4			systemic [cellular membrane, surface activity, polyamine]	2.8	unlikely	no
Benzoic acid	1	65-85-0	3, 4	C7H6O2		acid	2.5	unlikely	No
Bromoacetic acid	1	79-08-3	4	C2H3BrO2		acid, general chemical reactivity	2.5	likely	no

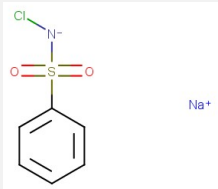
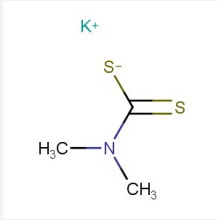
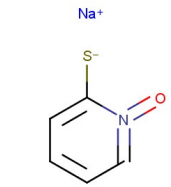
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Citric acid	1	77-92-9	2	C6H8O7		acid	2.5	unlikely	no
Decanoic acid	1	334-48-5	4	C10H20O2		acid, systemic [cellular membrane, surface activity]	2.5	unlikely	no
Nonanionic acid, pelargonic acid	1	112-05-0	2	C9H18O2		acid, systemic [cellular membrane, surface activity]	2.5	unlikely	no
Octanoic acid	1	124-07-2	4	C8H16O2		acid, systemic [cellular membrane, surface activity]	2.5	unlikely	no
Peracetic acid	1	79-21-0	1, 2, 3, 4, 5, 11, 12	C2H4O3		oxidation	2.2	likely	yes
Peracetic acid generated from tetra-acetylethylenediamine (TAED) and sodium percarbonate	1	79-21-0 (Peracetic acid)	2, 3, 4	C2H4O3 (Peracetic acid)		oxidation	2.2	likely	yes

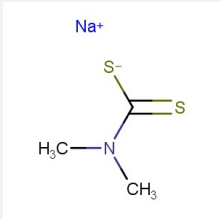
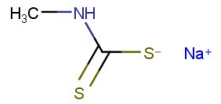
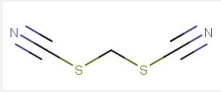
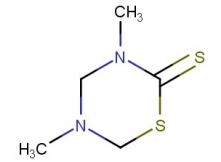
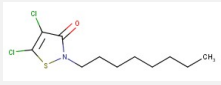
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
L-(+)-lactic acid	1	79-33-4	1, 2, 4	C3H6O3		acid	2.5	unlikely	no
Chlorocresol	1	59-50-7	1, 2, 3	C7H7ClO		systemic	2.4 / 2.11	unlikely	no
Biphenyl-2-ol	1	90-43-7	1, 2, 3, 4	C12H10O		systemic	2.4 / 2.11	unlikely	no
Propane-1-ol	1	71-23-8	1, 2, 4	C3H8O		alcohol	2.4	unlikely	no
Propane-2-ol	1	67-63-0	1, 2, 4	C3H8O		alcohol	2.4	unlikely	no

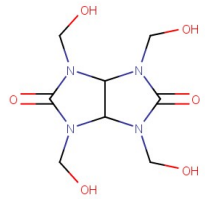
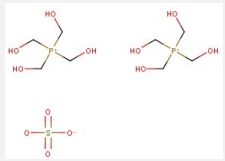
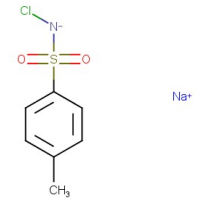
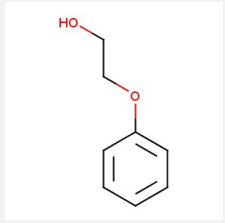
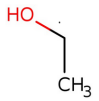
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Hydrogen peroxide	1	7722-84-1	1, 2, 3, 4, 5, 11, 12 (11 and 12: initial approval in progress)	H2O2		oxidation	2.2	likely	yes
Calcium dihydroxyde	1	1305-62-0	2, 3	Ca(OH)2	Ca2+ 2xOH-	base	2.6	unlikely	no
Calcium magnesium hydroxide	1	39445-23-3	2, 3	CaH4MgO4	Mg2+ Ca2+ 4xOH-	base	2.6	unlikely	no
Calcium magnesium oxide	1	37247-91-9	2, 3	CaMgO2	Mg2+ Ca2+ 2xO2-	base	2.6	unlikely	no
Calcium oxide	1	1305-78-8	2	CaO	Ca2+ O2-	base	2.6	unlikely	no
Copper sulphate pentahydrate	1	7758-99-8	2	CuO4S		systemic	2.6	unlikely	no
Glutaral (Glutaraldehyde)	1	111-30-8	2, 3, 4, 11, 12	C5H8O2		active carbonyl	2.3.1	likely	no
Iodine	1	7553-56-2	1, 3, 4	I2		halogene [iodination]	1.3	likely	no

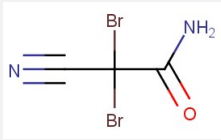
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Polyvinylpyrrolidone iodine	1	25655-41-8	1, 3, 4			halogene [iodination]	1.3	likely	no
Polyhexamethylene biguanide hydrochloride with a mean number-average molecular weight (Mn) of 1415 and a mean polydispersity (PDI) of 4.7 (PHMB(1415;4.7))	1	1802181-67-4	2, 4		~ 	systemic [cellular membrane, surface activity, polyamine]	2.11	unlikely	no
Polyhexamethylene biguanide hydrochloride with a mean number-average molecular weight (Mn) of 1600 and a mean polydispersity (PDI) of 1.8 (PHMB(1600;1.8))	1	27083-27-8	2, 3, 4, 11		~ 	systemic [cellular membrane, surface activity, polyamine]	2.11	unlikely	no
(Benzothiazol-2-ylthio)methyl thiocyanate (TCMBT)	2	21564-17-0	12	C9H6N2S3		systemic [isothiazolone]	2.7	unlikely	no
α,α',α''-Trimethyl-1,3,5-triazine-1,3,5(2H,4H,6H)-triethanol (HPT)	2	25254-50-6	2	C12H27N3O3		active carbonyl [formaldehyde release]	2.3.2	likely	no

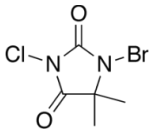
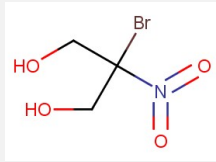
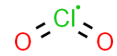
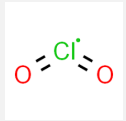
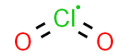
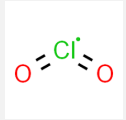
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
1,2-Benzisothiazol-3(2H)-one (BIT)	2	2634-33-5	2	C7H5NOS		systemic [isothiazolone]	2.7	unlikely	no
1-[2-(Allyloxy)-2-(2,4-dichlorophenyl)ethyl]-1H-imidazole	2	35554-44-0	3	C14H14Cl2N2O		systemic	2.11	unlikely	no
Octhilinone (ISO); 2-octyl-2H-isothiazol-3-one (OIT)	2	26530-20-1	11	C11H19NOS		systemic [isothiazolone]	2.7	unlikely	no
3,3'-Methylenebis[5-methyloxazolidine] (MBO)	2	66204-44-2	2, 11, 12	C9H18N2O2		active carbonyl [formaldehyde release]	2.3.2	likely	no
2,2',2''-(Hexahydro-1,3,5-triazine-1,3,5-triyl)triethanol (HHT)	2	4719-04-4	11, 12	C9H21N3O3		active carbonyl [formaldehyde release]	2.3.2	likely	no

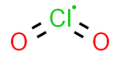
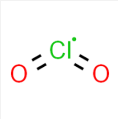
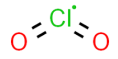
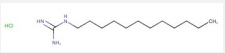
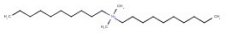
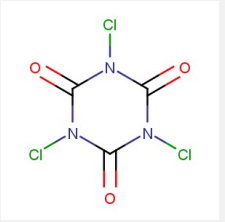
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Sodium N-chlorobenzenesulphonamide (Chloramine B)	2	127-52-6	2, 3, 4, 5	C6H5ClNNaO2S		halogene [chlorination]	1.1.1	likely	yes
Cyanamide	2	420-04-2	3	CH2N2		general chemical reactivity	2.11	likely	no
Potassium dimethyldithiocarbamate	2	128-03-0	11, 12	C3H6KNS2		systemic [enzyme inhibitor]	2.11	unlikely	no
Pyridine-2-thiol 1-oxide, sodium salt (Pyrithion)	2	3811-73-2	2	C5H4NNaOS		systemic	2.11	unlikely	no

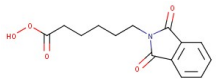
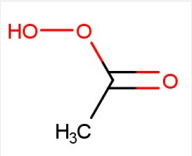
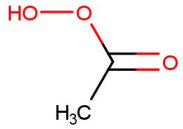
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Sodium dimethyldithiocarbamate (Dithocarb, DDTC)	2	128-04-1	11, 12	C3H6NNaS2		systemic [enzyme inhibitor]	2.11	unlikely	no
Metam sodium	2	137-42-8	11	C2H4NNaS2		systemic [enzyme inhibitor, MITC release]	2.10	unlikely	no
Methylene dithiocyanate	2	6317-18-6	12	C3H2N2S2		active carbonyl [formaldehyde release], systemic [enzyme inhibitor, MITC release]	2.10/2.3.1	likely	no
Dazomet	2	533-74-4	12	C5H10N2S2		active carbonyl [formaldehyde release], systemic [enzyme inhibitor, MITC release]	2.10/2.3.1	likely	no
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	2	64359-81-5	11	C11H17Cl2NOS		systemic, [isothiazolone]	2.7	unlikely	no

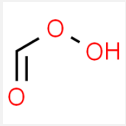
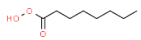
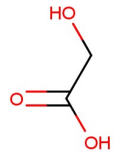
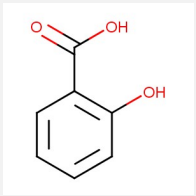
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazole-2,5(1H,3H)-dione (TMAD)	2	5395-50-6	2, 11, 12	C8H14N4O6		active carbonyl [formaldehyde release]	2.3.2	likely	no
Tetrakis(hydroxymethyl)phosphonium sulphate(2:1) (THPS)	2	55566-30-8	11, 12	C8H24O12P2S		systemic [cellular membrane, enzyme inhibitor]	2.11	unlikely	no
Tosylchloramide sodium (Chloramine T)	2	127-65-1	2, 3, 4, 5	C7H7ClNNaO2S		halogene [chlorination]	1.1.1	likely	yes
2-Phenoxyethanol	2	122-99-6	1, 2, 4	C8H10O2		systemic [cellular membrane, enzyme inhibitor]	2.4	unlikely	no
Ethanol	2	64-17-5	1, 2, 4	C2H6O		alcohol	2.4	unlikely	no

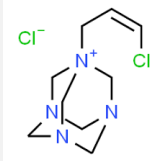
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
2,2-dibromo-2-cyanoacetamide (DBNPA)	2	10222-01-2	2, 4, 11, 12	C3H2Br2N2O		halogene [acts similar to the typical halogen biocides]	1.2.1	likely	yes
Active bromine generated from bromine chloride	2	7726-95-6	11	Br2	Br—Br	halogene [bromination]	1.2.2	likely	yes
Active bromine generated from sodium bromide and calcium hypochlorite	2	7726-95-6	2, 11, 12	Br2	Br—Br	halogene [bromination]	1.2.2	likely	yes
Active bromine generated from ozone and bromide of natural water and sodium bromide	2	7726-95-6	2	Br2	Br—Br	halogene [bromination]	1.2.2	likely	yes
Active bromine generated from sodium bromide and chlorine	2	7726-95-6	2, 11, 12	Br2	Br—Br	halogene [bromination]	1.2.2	likely	yes
Active bromine generated from sodium bromide and sodium hypochlorite	2	7726-95-6	2, 11, 12	Br2	Br—Br	halogene [bromination]	1.2.2	likely	yes
Active bromine generated from sodium bromide by electrolysis	2	7726-95-6	2, 11, 12	Br2	Br—Br	halogene [bromination]	1.2.2	likely	yes
Active chlorine originating from different sources	2	7782-50-5	1, 2, 3, 4, 5, 11, 12	Cl2	Cl—Cl	halogene [chlorination]	1.1.3	likely	yes
Ammonium bromide	2	12124-97-9	11, 12	NH4Br	NH4+ Br-	systemic	2.6	unlikely	no

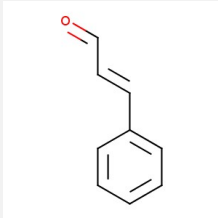
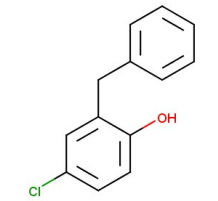
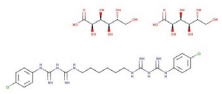
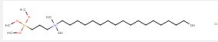
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Bromochloro-5,5-dimethylimidazolidine-2,4-dione (BCDMH)	2	32718-18-6	2, 11, 12			halogene [chlorination, bromination]	1.1.1/1.2.1	likely	yes
2-Bromo-2-nitro-1,3-diol (Bronopol)	2	52-51-7	2, 11, 12	C3H6BrNO4		systemic, [enzyme inhibitor]	2.11	unlikely	no
Chlorine dioxide	2	10049-04-4	2, 3, 4, 5	ClO2		oxidation, halogene [chlorination]	1.5	likely	yes
Chlorine dioxide generated from sodium chlorate and hydrogen peroxide in the presence of a strong acid	2	10049-04-4	2, 3, 4, 5, 11, 12	ClO2		oxidation, halogene [chlorination]	1.5	likely	yes
Chlorine dioxide generated from sodium chlorite and sodium bisulfate	2	10049-04-4	2, 3, 4, 5, 11, 12	ClO2		oxidation, halogene [chlorination]	1.5	likely	yes
Chlorine dioxide generated from sodium chlorite by acidification	2	10049-04-4	2, 3, 4, 5, 11, 12	ClO2		oxidation, halogene [chlorination]	1.5	likely	yes

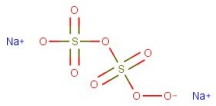
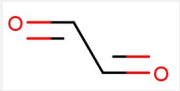
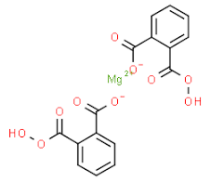
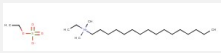
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Chlorine dioxide generated from sodium chlorite by electrolysis	2	10049-04-4	2, 3, 4, 5, 11, 12	ClO2		oxidation, halogene [chlorination]	1.5	likely	yes
Chlorine dioxide generated from sodium chlorite by oxidation	2	10049-04-4	2, 3, 4, 5, 11, 12	ClO2		oxidation, halogene [chlorination]	1.5	likely	yes
Chlorine dioxide generated from Tetrachlorodecaoxide complex (TCDO) by acidification	2	92047-76-2	2, 4	ClO2		oxidation, halogene [chlorination]	1.5	likely	yes
Dodecylguanidine monohydrochloride	2	13590-97-1	11	C13H30ClN3		systemic [cellular membrane, surface activity, polyamine]	2.11	unlikely	no
Didecyldimethylammonium chloride (DDAC)	2	7173-51-5	1, 2, 3, 4, 11, 12	C22H48ClN		systemic [cellular membrane, surface activity, quaternary ammonium]	2.8	unlikely	no
1,2,3 Trichlorisocyanursäure (Symclosene)	2	87-90-1	2, 3, 4, 5, 11, 12	C3Cl3N3O3		halogene [chlorination]	1.1.1	likely	yes

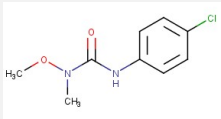
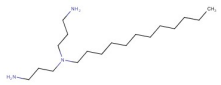
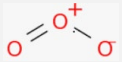
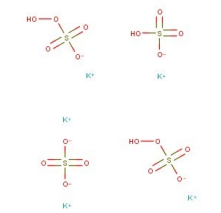
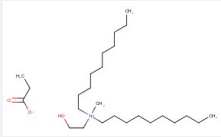
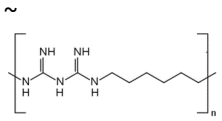
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Monochloramine generated from ammonia and a chlorine source	2	10599-90-3	5, 11	ClH2N		chloramine [chlorination]	1.4	likely	yes
Monochloramine generated from ammonium carbamate and a chlorine source	2	10599-90-3	11, 12	ClH2N		chloramine [chlorination]	1.4	likely	yes
Monochloramine generated from ammonium chloride and a chlorine source	2	10599-90-3	11, 12	ClH2N		chloramine [chlorination]	1.4	likely	yes
Monochloramine generated from ammonium hydroxide and a chlorine source	2	10599-90-3	5	ClH2N		chloramine [chlorination]	1.4	likely	yes
6-(Phthalimido) peroxyhexanoic acid	2	128275-31-0	1, 2	C14H15NO5		oxidation [peroxide]	2.2	likely	Yes
Peracetic acid generated by perhydrolysis of N-acetylcaprolactam by hydrogen peroxide in alkaline conditions	2	79-21-0 (Peracetic acid)	2	C2H4O3		oxidation [peroxide]	2.2	likely	Yes
Peracetic acid generated from 1,3-diacetyloxypropan-2-yl acetate and hydrogen peroxide	2	79-21-0 (Peracetic acid)	4	C2H4O3		oxidation [peroxide]	2.2	likely	Yes

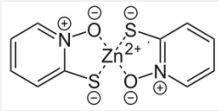
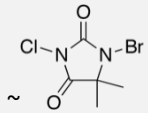
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Performic acid generated from formic acid and hydrogen peroxide	2	107-32-4	2, 3, 4, 5, 11, 12	CH2O3		oxidation [peroxide]	2.2	likely	Yes
Peroxyoctanoic acid	2	33734-57-5	2, 3, 4	C8H16O3		oxidation [peroxide]	2.2	likely	Yes
Formic acid	2	64-18-6	2, 3, 4, 5, 11, 12	CH2O2		acid	2.5	unlikely	no
Glycollic acid	2	79-14-1	2, 3, 4	C2H4O3		acid	2.5	unlikely	no
Salicylic acid	2	69-72-7	2, 3, 4	C7H6O3		acid	2.5	unlikely	no
Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl, chlorides (ADBAC)	2	68391-01-5	1, 2, 3, 4, 11, 12			systemic, [cellular membrane; quaternary ammonium]	2.8	unlikely	no

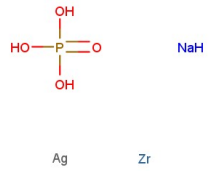
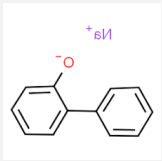
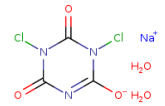
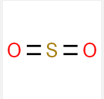
Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Quaternary ammonium compounds, C12-14-alkyl[(ethylphenyl)methyl]dimethyl, chlorides	2	85409-23-0	1, 2, 3, 4, 11, 12			systemic, [cellular membrane; quaternary ammonium]	2.8	unlikely	no
Quaternary ammonium compounds, benzyl-C12-14-alkyldimethyl, chlorides	2	85409-22-9	1, 2, 3, 4, 11, 12			systemic, [cellular membrane; quaternary ammonium]	2.8	unlikely	no
Quaternary ammonium compounds, di-C8-10-alkyldimethyl, chlorides	2	68424-95-3	1, 2, 3, 4, 11, 12			systemic, [cellular membrane; quaternary ammonium]	2.8	unlikely	no
Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl, salts with 1,2-benzisothiazol-3(2H)-one 1,1-dioxide (1:1)	2	68989-01-5	2, 4			systemic, [cellular membrane; quaternary ammonium; isothiazolone]	2.8	unlikely	no
Methenamine 3-chloroallylochloride (CTAC)	2	4080-31-3	12	C9H16Cl2N4		systemic, [cellular membrane; quarternary ammonium]	2.8	unlikely	no
Amines, C10-16-alkyldimethyl, N-oxides	2	70592-80-2	4			systemic, [cellular membrane; quaternary ammonium]	2.8	unlikely	no

Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Cinnamaldehyde	2	104-55-2	2	C9H8O		active carbonyl	2.3.1	likely	no
2-Benzyl-4-chlorphenol (Clorofene)	2	120-32-1	2	C13H11ClO		systemic	2.4 / 2.11	unlikely	no
Copper	2	7440-50-8	2, 5, 11	Cu		systemic	2.6	unlikely	no
D-gluconic acid, compound with N,N''-bis(4-chlorophenyl)-3,12-diimino-2,4,11,13-tetraazatetradecanediamidine (2:1), (Chlorhexidin digluconat, CHDG)	2	18472-51-0	1, 2, 3	C34H54Cl2N10O14		systemic [cellular membrane, surface activity, polyamine]	2.11	unlikely	no
Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DTSACl)	2	27668-52-6	2	C26H58ClNO3Si		systemic [cellular membrane, surface activity, quaternary ammonium]	2.8	unlikely	no

Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Disodium peroxodisulphate	2	7775-27-1	4	Na2O8S2		oxidation [peroxide]	2.2	likely	yes
Formaldehyde	2	50-00-0	2, 3	CH2O		active carbonyl [formaldehyde release]	2.3.1	likely	no
Free radicals generated in situ from ambient air or water	2		2, 3, 4, 5, 11, 12			oxidation	2.11	likely	no
Glyoxal	2	107-22-2	2, 3, 4	C2H2O2		active carbonyl	2.3.1	likely	no
Dihydrogen bis[monoperoxyphthalato(2-)-O1,OO1]magnesate(2-), magnesium monoperoxyphthalate (MMPP)	2	78948-87-5	2	C16H10MgO10		oxidation [peroxide]	2.2	likely	yes
Mecetronium etilsulfate (MES)	2	3006_10_08	1	C22H49NO4S		systemic [cellular membrane, surface activity, quaternary ammonium]	2.8	unlikely	no
Ammonium sulphate	2	7783-20-2	11, 12	H8N2O4S		systemic	2.6	unlikely	no

Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Monolinuron	2	1746-81-2	2	C9H11ClN2O2		systemic	2.11	unlikely	no
N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine	2	2372-82-9	2, 3, 4, 11, 12	C18H41N3		systemic [cellular membrane, surface activity, polyamine]	2.11	unlikely	no
Ozone	2	10028-15-6	2, 4, 5, 11	O3		oxidation	2.1	likely	yes
Pentapotassium bis(peroxymonosulphate) bis(sulphate)	2	70693-62-8	2, 3, 4, 5	H3K5O18S4		oxidation [peroxide]	2.2	likely	yes
Poly(oxy-1,2-ethanediyl), .alpha.-[2-(dide cylmethylammonio)ethyl]-.omega.- hydroxy-, propanoate (salt) (Bardap 26)	2	94667-33-1	2, 4	C26H55NO3		systemic [cellular membrane, surface activity, quaternary ammonium]	2.8	unlikely	no
Polyhexamethylene biguanide hydrochloride with a mean number-average molecular weight (Mn) of 1415 and a mean polydispersity (PDI) of 4.7 (PHMB (1415; 4.7))	2	1802181-67-4	3, 11			systemic [cellular membrane, surface activity, polyamine]	2.11	unlikely	no

Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Pyrithione zinc	2	13463-41-7	2	C10H8N2O2S2Zn		systemic	2.11	unlikely	no
Reaction mass of titanium dioxide and silver chloride	2		1, 2, 4, 11			systemic [silver]	2.9	unlikely	no
Reaction products of 5,5-dimethylhydantoin, 5-ethyl-5-methylhydantoin with bromine and chlorine ("BCDMH/BCMEH")	2		11			Chlorination, Bromination [Halogene]	1.1.1/1.2.1	likely	yes
Reaction products of: glutamic acid and N-(C12-14-alkyl)propylenediamine (Glucoprotamin)	2	164907-72-6	2, 4			systemic [cellular membrane, surface activity, polyamine]	2.11	unlikely	no
Silver	2	7440-22-4	2, 4, 5, 11	Ag		systemic [silver]	2.9	unlikely	no
Silver chloride	2	7783-90-6	11	AgCl	$Ag^+ Cl^-$	systemic [silver]	2.9	unlikely	no
Silver copper zeolite	2	130328-19-7	2, 4			systemic [silver]	2.9	unlikely	
Silver nitrate	2	7761-88-8	1, 2, 3, 4, 5, 11	AgNO3	$Ag^+ NO_3^-$	systemic [silver]	2.9	unlikely	no
Silver phosphate glass	2	308069-39-8	2			systemic [silver]	2.9	unlikely	no

Substance name	Status*	CAS-number	PT	Molecular formula	Chemical structure	Mode of action [details]	Categorisation according to chemical structure	DBP-formation potential	Known DBPs
Silver sodium zirconium hydrogenphosphate	2	265647-11-8; 155925-27-2	1, 2, 4	AgH4NaO4PZr		systemic [silver]	2.9	unlikely	no
Silver zeolite	2	130328-18-6	2, 4, 5			systemic [silver]	2.9	unlikely	no
Silver zinc zeolite	2	130328-20-0	2, 4			systemic [silver]	2.9	unlikely	no
Sodium 2-biphenylate	2	132-27-4	4	C12H9NaO		systemic, base	2.4 / 2.11	unlikely	no
Sodium dichloroisocyanurate dihydrate (Troclosene sodium)	2	51580-86-0	2, 3, 4, 5, 11, 12	C3Cl2N3NaO		halogene [chlorination]	1.1.1	likely	no
sulphur oxide generated from sulphur by combustion	2	7446-09-5	4	SO2		general chemical reactivity	2.6	likely	no

* Explanation for the coding in the column:

1: approved 2: initial approval in process

C Detailed results of calculated distribution of the biocidal a.s. and DBP in different compartments

Hydrogen peroxide

Table 24: Distribution for hydrogen peroxide and selected DBP for the scenario "large water voume during use"

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
007722-84-1	**Hydrogen peroxide**	**100.00**	**4.57**	-	-	-
000598-70-9	Acetamide, 2,2-dibromo-	100.00	21.92	No	Yes	different
000075-96-7	Acetic acid, tribromo-	100.00	27.49	No	Yes	different
000079-43-6	Acetic acid, dichloro-	100.00	12.17	No	No	comparable
000079-11-8	Acetic acid, chloro-	100.00	5.38	No	No	comparable
000106-41-2	Phenol, 4-bromo-	100.00	0.00	No	No	comparable
003252-43-5	Acetonitrile, dibromo-	99.99	53.13	No	Yes	different
083463-62-1	Bromochloracetonitrile	99.98	50.27	No	Yes	different
000545-06-2	Acetonitrile, trichloro-	99.98	89.92	No	Yes	different
003018-12-0	Dichloroacetonitrile	99.94	47.40	No	Yes	different
000621-64-7	1-Propanamine, N-nitroso-N-propyl-	99.91	56.35	No	Yes	different
000075-25-2	Methane, tribromo-	91.95	77.50	No	Yes	different
000124-48-1	Methane, dibromochloro-	88.66	71.39	Yes	Yes	different
000075-27-4	Methane, bromodichloro-	74.25	64.38	Yes	Yes	different
000067-66-3	Methane, trichloro-	62.50	54.43	Yes	Yes	different

Table 25: Distribution for hydrogen peroxide and selected DBP for the scenario "small water volume during use"

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
007722-84-1	**Hydrogen peroxide**	**98.22**	**4.57**	-	-	-
000598-70-9	Acetamide, 2,2-dibromo-	99.96	21.92	No	Yes	different
000075-96-7	Acetic acid, tribromo-	99.19	27.49	No	Yes	different

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000079-43-6	Acetic acid, dichloro-	97.98	12.17	No	No	comparable
000079-11-8	Acetic acid, chloro-	97.78	5.38	No	No	comparable
000106-41-2	Phenol, 4-bromo-	72.95	0.00	No	Yes	different
003252-43-5	Acetonitrile, dibromo-	50.11	53.13	Yes	Yes	different
083463-62-1	Bromochloracetonitrile	24.74	50.27	Yes	Yes	different
000545-06-2	Acetonitrile, trichloro-	23.31	89.92	Yes	Yes	different
003018-12-0	Dichloroacetonitrile	9.72	47.40	Yes	Yes	different
000621-64-7	1-Propanamine, N-nitroso-N-propyl-	7.05	56.35	Yes	Yes	different
000075-25-2	Methane, tribromo-	0.08	77.50	Yes	Yes	different
000124-48-1	Methane, dibromochloro-	0.05	71.39	Yes	Yes	different
000075-27-4	Methane, bromodichloro-	0.02	64.38	Yes	Yes	different
000067-66-3	Methane, trichloro-	0.01	54.43	Yes	Yes	different

Hypobromite

Table 26: Distribution for hypobromite and selected DBP for the scenario “large water voume during use”

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
13824-96-9	**Hypobromite**	**100.00**	**0.00**			
003252-43-5	Acetonitrile, dibromo-	99.99	53.13	No	Yes	different
000598-91-4	Methane, dibromonitro-	74.25	64.38	Yes	Yes	different

Table 27: Distribution for hypobromite and selected DBP for the scenario “small water voume during use”

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
13824-96-9	**Hypobromite**	**71.33**	**0.00**			
003252-43-5	Acetonitrile, dibromo-	50.11	53.13	Yes	Yes	different

CAS	Substance	In water/air (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000598-91-4	Methane, dibromonitro-	0.02	64.38	Yes	Yes	different

Chlorine dioxide

Table 28: Distribution for chlorine dioxide and selected DBP for the scenario "large water volume during use"

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
10049-04-4	**Chlorine dioxide**	**85.96**	**0.00**	-	-	-
000107-22-2	Ethanedial	100.00	1.05	Yes	No	different
071133-14-7	Bromodichloroacetic acid	100.00	23.17	Yes	Yes	different
000079-43-6	Acetic acid, dichloro-	100.00	12.17	Yes	Yes	different
000079-11-8	Acetic acid, chloro-	100.00	5.38	Yes	No	different
000076-03-9	Acetic acid, trichloro-	100.00	5.65	Yes	No	different
000050-00-0	Formaldehyde	99.99	18.87	Yes	Yes	different
000632-21-3	2-Propane, 1,1,3,3-tetrachloro-	99.99	46.92	Yes	Yes	different
083463-62-1	Bromochloracetonitrile	99.98	50.27	Yes	Yes	different
010595-95-6	N-Nitrosomethylethylamine	99.96	19.37	Yes	Yes	different
003018-12-0	Dichloroacetonitrile	99.94	47.40	Yes	Yes	different
000100-52-7	Benzaldehyde	99.57	49.51	Yes	Yes	different
000075-47-8	Methane, triiodo-	99.50	92.74	Yes	Yes	different
000075-07-0	Acetaldehyde	98.92	8.81	Yes	No	different
000123-38-6	Propanal	98.81	23.99	Yes	Yes	different
034970-00-8	Bromochloroiodomethane	96.48	67.02	Yes	Yes	different
018829-56-6	2-Nonenal, (E)-	96.36	88.01	Yes	Yes	different
000090-12-0	Naphthalene, methyl-	92.24	98.57	No	Yes	different
000075-25-2	Methane, tribromo-	91.95	77.50	No	Yes	different
000594-04-7	Dichloroiodomethane	89.97	63.40	No	Yes	different
000124-48-1	Methane, dibromochloro-	88.66	71.39	No	Yes	different
000593-71-5	Chloroiodomethane	87.52	54.23	No	Yes	different

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000112-31-2	Decanal	77.25	94.71	No	Yes	different
000076-06-2	Methane, trichloronitro-	74.91	0.00	Yes	No	different
000075-27-4	Methane, bromodichloro-	74.25	64.38	Yes	Yes	different
000067-66-3	Methane, trichloro-	62.50	54.43	Yes	Yes	different

Table 29: Distribution for chlorine dioxide and selected DBP for the scenario "small water volume during use"

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
10049-04-4	**Chlorine dioxide**	**0.04**	**0.00**	-	-	-
000107-22-2	Ethanedial	99.19	1.05	Yes	No	different
071133-14-7	Bromodichloroacetic acid	98.12	23.17	Yes	Yes	different
000079-43-6	Acetic acid, dichloro-	97.98	12.17	Yes	Yes	different
000079-11-8	Acetic acid, chloro-	97.78	5.38	Yes	No	different
000076-03-9	Acetic acid, trichloro-	96.79	5.65	Yes	No	different
000050-00-0	Formaldehyde	54.75	18.87	Yes	Yes	different
000632-21-3	2-Propane, 1,1,3,3-tetrachloro-	34.83	46.92	Yes	Yes	different
083463-62-1	Bromochloracetonitrile	24.74	50.27	Yes	Yes	different
010595-95-6	N-Nitrosomethylethylamine	12.99	19.37	Yes	Yes	different
003018-12-0	Dichloroacetonitrile	9.72	47.40	Yes	Yes	different
000100-52-7	Benzaldehyde	1.50	49.51	No	Yes	different
000075-47-8	Methane, triiodo-	1.32	92.74	No	Yes	different
000075-07-0	Acetaldehyde	0.61	8.81	No	No	comparable
000123-38-6	Propanal	0.55	23.99	No	Yes	different
034970-00-8	Bromochloroiodomethane	0.18	67.02	No	Yes	different
018829-56-6	2-Nonenal, (E)-	0.18	88.01	No	Yes	different
000090-12-0	Naphthalene, methyl-	0.08	98.57	No	Yes	different
000075-25-2	Methane, tribromo-	0.08	77.50	No	Yes	different
000594-04-7	Dichloroiodomethane	0.06	63.40	No	Yes	different
000124-48-1	Methane, dibromochloro-	0.05	71.39	No	Yes	different

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000593-71-5	Chloroiodomethane	0.05	54.23	No	Yes	different
000112-31-2	Decanal	0.02	94.71	No	Yes	different
000076-06-2	Methane, trichloronitro-	0.02	0.00	No	No	comparable
000075-27-4	Methane, bromodichloro-	0.02	64.38	No	Yes	different
000067-66-3	Methane, trichloro-	0.01	54.43	No	Yes	different

Ozone

Table 30: Distribution for ozone and selected DBP for the scenario "large water volume during use"

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
010028-15-6	**Ozone**	**6.30**	**0.52**	-	-	-
000084-65-1	9,10-Anthracenedione	100.00	99.34	Yes	Yes	different
000099-06-9	Benzoic acid, 3-hydroxy-	100.00	29.87	Yes	Yes	different
000598-70-9	Acetamide, 2,2-dibromo-	100.00	21.92	Yes	Yes	different
000062-23-7	Benzoic acid, 4-nitro-	100.00	44.12	Yes	Yes	different
000075-87-6	Acetaldehyde, trichloro-	100.00	34.45	Yes	Yes	different
000107-22-2	Ethanedial	100.00	1.05	Yes	No	different
000075-96-7	Acetic acid, tribromo-	100.00	27.49	Yes	Yes	different
000069-72-7	Benzoic acid, 2-hydroxy-	100.00	52.86	Yes	Yes	different
000079-43-6	Acetic acid, dichloro-	100.00	12.17	Yes	Yes	different
000079-11-8	Acetic acid, chloro-	100.00	5.38	Yes	No	different
000076-03-9	Acetic acid, trichloro-	100.00	5.65	Yes	No	different
000059-89-2	N-Nitrosomorpholine	100.00	9.57	Yes	No	different
000050-00-0	Formaldehyde	99.99	18.87	Yes	Yes	different
000100-75-4	Piperidine, 1-nitroso-	99.99	26.54	Yes	Yes	different
003039-13-2	Acetaldehyde, dibromo-	99.99	20.90	Yes	Yes	different
083463-62-1	Bromochloracetonitrile	99.98	50.27	Yes	Yes	different
000545-06-2	Acetonitrile, trichloro-	99.98	89.92	Yes	Yes	different
023676-09-7	Ethyl 4-ethoxybenzoate	99.94	96.03	Yes	Yes	different
003018-12-0	Dichloroacetonitrile	99.94	47.40	Yes	Yes	different

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000563-70-2	Bromonitromethane	99.92	0.00	Yes	No	different
007119-89-3	Methane, dichloronitro	99.91	0.00	Yes	No	different
000079-02-7	Acetaldehyde, dichloro-	99.86	17.36	Yes	Yes	different
000143-07-7	Dodecanoic acid	99.85	93.77	Yes	Yes	different
000098-86-2	Ethanone, 1-phenyl-	99.83	65.43	Yes	Yes	different
000107-14-2	Acetonitrile, chloro-	99.82	52.49	Yes	Yes	different
000924-16-3	1-Butanamine, N-butyl-N-nitroso-	99.78	86.68	Yes	Yes	different
001794-84-9	Methane, chloronitro-	99.76	0.00	Yes	No	different
000107-20-0	Acetaldehyde, chloro-	99.61	14.31	Yes	Yes	different
000100-52-7	Benzaldehyde	99.57	49.51	Yes	Yes	different
000075-47-8	Methane, triiodo-	99.50	92.74	Yes	Yes	different
000075-07-0	Acetaldehyde	98.92	8.81	Yes	No	different
000593-94-2	Dibromoiodomethane	98.82	70.87	Yes	Yes	different
000123-38-6	Propanal	98.81	23.99	Yes	Yes	different
000132-64-9	Dibenzofuran	96.63	99.59	Yes	Yes	different
034970-00-8	Bromochloroiodomethane	96.48	67.02	Yes	Yes	different
018829-56-6	2-Nonenal, (E)-	96.36	88.01	Yes	Yes	different
000090-12-0	Naphthalene, methyl-	92.24	98.57	Yes	Yes	different
000075-25-2	Methane, tribromo-	91.95	77.50	Yes	Yes	different
000594-04-7	Dichloroiodomethane	89.97	63.40	Yes	Yes	different
000124-48-1	Methane, dibromochloro-	88.66	71.39	Yes	Yes	different
000112-31-2	Decanal	77.25	94.71	Yes	Yes	different
000076-06-2	Methane, trichloronitro-	74.91	0.00	Yes	No	different
000075-27-4	Methane, bromodichloro-	74.25	64.38	Yes	Yes	different
000683-72-7	2,2-dichloroacetamide	66.56	71.78	Yes	Yes	different
000067-66-3	Methane, trichloro-	62.50	54.43	Yes	Yes	different

Table 31: Distribution for ozone and selected DBP for the scenario "small water volume during use"

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
010028-15-6	**Ozone**	**0.00**	**0.52**	-	-	-
000084-65-1	9,10-Anthracenedione	100.00	99.34	Yes	Yes	different
000099-06-9	Benzoic acid, 3-hydroxy-	100.00	29.87	Yes	Yes	different
000598-70-9	Acetamide, 2,2-dibromo-	99.96	21.92	Yes	Yes	different
000062-23-7	Benzoic acid, 4-nitro-	99.90	44.12	Yes	Yes	different
000075-87-6	Acetaldehyde, trichloro-	99.29	34.45	Yes	Yes	different
000107-22-2	Ethanedial	99.19	1.05	Yes	No	different
000075-96-7	Acetic acid, tribromo-	99.19	27.49	Yes	Yes	different
000069-72-7	Benzoic acid, 2-hydroxy-	98.23	52.86	Yes	Yes	different
000079-43-6	Acetic acid, dichloro-	97.98	12.17	Yes	Yes	different
000079-11-8	Acetic acid, chloro-	97.78	5.38	Yes	No	different
000076-03-9	Acetic acid, trichloro-	96.79	5.65	Yes	No	different
000059-89-2	N-Nitrosomorpholine	94.33	9.57	Yes	No	different
000050-00-0	Formaldehyde	54.75	18.87	Yes	Yes	different
000100-75-4	Piperidine, 1-nitroso-	32.56	26.54	Yes	Yes	different
003039-13-2	Acetaldehyde, dibromo-	31.16	20.90	Yes	Yes	different
083463-62-1	Bromochloracetonitrile	24.74	50.27	Yes	Yes	different
000545-06-2	Acetonitrile, trichloro-	23.31	89.92	Yes	Yes	different
023676-09-7	Ethyl 4-ethoxybenzoate	10.13	96.03	Yes	Yes	different
003018-12-0	Dichloroacetonitrile	9.72	47.40	No	Yes	different
000563-70-2	Bromonitromethane	7.76	0.00	No	No	comparable
007119-89-3	Methane, dichloronitro	7.23	0.00	No	No	comparable
000079-02-7	Acetaldehyde, dichloro-	4.62	17.36	No	Yes	different
000143-07-7	Dodecanoic acid	4.20	93.77	No	Yes	different
000098-86-2	Ethanone, 1-phenyl-	3.77	65.43	No	Yes	different
000107-14-2	Acetonitrile, chloro-	3.64	52.49	No	Yes	different
000924-16-3	1-Butanamine, N-butyl-N-nitroso-	3.00	86.68	No	Yes	different
001794-84-9	Methane, chloronitro-	2.68	0.00	No	No	comparable
000107-20-0	Acetaldehyde, chloro-	1.68	14.31	No	Yes	different

CAS	Substance	In water (%)	In sludge (%)	Diff. in water/air	Diff. in sludge	Conclusion
000100-52-7	Benzaldehyde	1.50	49.51	No	Yes	different
000075-47-8	Methane, triiodo-	1.32	92.74	No	Yes	different
000075-07-0	Acetaldehyde	0.61	8.81	No	No	comparable
000593-94-2	Dibromoiodomethane	0.56	70.87	No	Yes	different
000123-38-6	Propanal	0.55	23.99	No	Yes	different
000132-64-9	Dibenzofuran	0.19	99.59	No	Yes	different
034970-00-8	Bromochloroiodomethane	0.18	67.02	No	Yes	different
018829-56-6	2-Nonenal, (E)-	0.18	88.01	No	Yes	different
000090-12-0	Naphthalene, methyl-	0.08	98.57	No	Yes	different
000075-25-2	Methane, tribromo-	0.08	77.50	No	Yes	different
000594-04-7	Dichloroiodomethane	0.06	63.40	No	Yes	different
000124-48-1	Methane, dibromochloro-	0.05	71.39	No	Yes	different
000112-31-2	Decanal	0.02	94.71	No	Yes	different
000076-06-2	Methane, trichloronitro-	0.02	0.00	No	No	comparable
000075-27-4	Methane, bromodichloro-	0.02	64.38	No	Yes	different
000683-72-7	2,2-dichloroacetamide	0.01	71.78	No	Yes	different
000067-66-3	Methane, trichloro-	0.01	54.43	No	Yes	different

D Detailed results of DBP analyses

Analytical control experiments

Table 32: Analysis of background signals (in µg/L) present in the matrices or induced by the application process determined by LC-MS

Substance	Matrices		Application solutions		
	Swimming pool	General	Hypo-chlorite	Hypo-bromite	Chlor-amine T
HAA					
Monochloroacetic acid	0.97	n.d.	n.d.	n.d.	0.54
Dichloroacetic acid	< LOD	0	5.97	n.d.	1.13
Trichloroacetic acid	n.d.	n.d.	5.76	n.d.	0.56
Monobromoacetic acid	0.82	1.40	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	< LOD	n.d.	n.d.	0.82	n.d.
Bromodichloroacetic acid	n.d.	n.d.	< LOD	n.d.	n.d.
Tribromoacetic acid	n.d.	n.d.	n.d.	6.77	n.d.
Iodacetic acid	n.d.	n.d.	< LOD	n.d.	n.d.
Bromochloroacetic acid	n.d.	n.d.	< LOD	0	< LOD
Other haloacids					
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	< LOD
Halobenzochinones					
2,6-dichloro-1,4-benzoquinone	< LOD	< LOD	1.61	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated					
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	0.87	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	126	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	0.32	n.d.
Non halogenated					
Phthalimide	n.d.	< LOD	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	n.d.	n.d.	< LOD	n.d.
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	0.17	21.1	n.d.	n.d.	n.d.

Substance	Matrices		Application solutions		
	Swimming pool	General	Hypo-chlorite	Hypo-bromite	Chlor-amine T
Acetophenon	0.74	0.78	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	< LOD	n.d.
Salicylic acid	< LOD	< LOD	n.d.	n.d.	n.d.
Propanal	12.15	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	0.36	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.

Table 33: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypochlorite by LC-MS – reproducibility in 5 replicates

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
HAA						
Monochloroacetic acid	n.d.	2.90	0.44	0.61	0.36	0.20
Dichloroacetic acid	1.83	54.2	55.1	57.2	56.7	60.0
Trichloroacetic acid	12.1	7.07	6.20	6.35	7.04	7.88
Monobromoacetic acid	4.56	< LOD	0.21	0.47	0.20	0.22
Dibromoacetic acid	0.84	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	2.19	1.24	1.37	1.25	1.29	1.22
Bromodichloroacetic acid	1.18	3.68	4.89	4.36	4.59	4.47
Tribromoacetic acid	1.12	< LOD	< LOD	< LOD	< LOD	< LOD
Iodacetic acid	n.d.	n.d.	< LOD	n.d.	< LOD	n.d.
Bromochloroacetic acid	1.75	20.7	20.2	20.3	20.9	20.4
Other haloacids						
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones						
2,6-dichloro-1,4-benzoquinone	0.32	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	0.21	n.d.	n.d.	n.d.	n.d.
Non halogenated						

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	< LOD	< LOD	0.20	< LOD	0.21
Decanal	n.d.	0.29	< LOD	n.d.	< LOD	n.d.
Acetaldehyde	0.94	< LOD	n.d.	n.d.	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD
Salicylic acid	0.25	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	n.d.	1.07	0.74	1.47	1.47	1.33
Benzaldehyde	1.25	< LOD	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.

Table 34: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypobromite by LC-MS – reproducibility in 5 replicates

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
HAA						
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	n.d.	< LOD	< LOD	< LOD	18.8	< LOD
Trichloroacetic acid	n.d.	< LOD	n.d.	< LOD	29.2	n.d.
Monobromoacetic acid	n.d.	0.61	< LOD	0.24	0.58	0.50
Dibromoacetic acid	181	513	489	478	486	387
Dibromochloroacetic acid	0.21	n.d.	n.d.	n.d.	n.d.	< LOD
Bromodichloroacetic acid	n.d.	1.06	1.05	1.70	1.07	1.44
Tribromoacetic acid	145	195	181	196	159	181
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	2.58	1.33	1.11	1.24	1.20	1.36
Other haloacids						
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones						
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	< LOD	n.d.	< LOD
Non halogenated						
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Decanal	< LOD	n.d.	n.d.	< LOD	n.d.	n.d.
Acetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
4-Nitrobenzoic acid	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD
Salicylic acid	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	11.1	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 35: Analysis of DBPs (in µg/L) after disinfection of general matrix in aqueous solution with sodium hypochlorite by LC-MS – reproducibility in 5 replicates

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
HAA						
Monochloroacetic acid	15.3	45.3	42.5	46.0	42.8	41.5
Dichloroacetic acid	290	351	341	329	347	270
Trichloroacetic acid	328	242	234	212	253	228
Monobromoacetic acid	n.d.	0.24	< LOD	0.28	0.28	0.28
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	1.50	n.d.	2.58	1.70	n.d.
Bromodichloroacetic acid	n.d.	18.5	0.98	28.2	13.7	0.59
Tribromoacetic acid	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	< LOD	21.0	2.00	31.0	22.5	1.30
Other haloacids						

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
2,2-dichloropropanoic acid/Dalapon	0.69	1.20	0.90	0.80	0.86	1.02
Halobenzochinones						
2,6-dichloro-1,4-benzoquinone	0.79	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
Non halogenated						
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.
Benzophenone	n.d.	n.d.	n.d.	< LOD	< LOD	< LOD
Decanal	n.d.	n.d.	n.d.	n.d.	0.40	n.d.
Acetaldehyde	167	149	167	166	166	166
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD
Salicylic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	0.50	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	17.5	3.76	5.76	6.29	7.43	6.75
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 36: Analysis of DBPs (in µg/L) after disinfection of general matrix in aqueous solution with hydrogen peroxide by LC-MS – reproducibility in 5 replicates

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
HAA						
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	< LOD	< LOD	< LOD	< LOD	< LOD	0.52
Trichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Monobromoacetic acid	n.d.	0.59	0.49	0.22	n.d.	n.d.

Substance	Reproducibility					
	Original experiment	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromodichloroacetic acid	n.d.	< LOD	< LOD	n.d.	n.d.	n.d.
Tribromoacetic acid	n.d.	< LOD	< LOD	n.d.	n.d.	< LOD
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other haloacids						
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones						
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated						
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	< LOD	< LOD
Benzophenone	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD
Decanal	n.d.	2.33	n.d.	n.d.	n.d.	< LOD
Acetaldehyde	1.31	8.69	8.56	7.78	7.90	8.55
Acetophenon	n.d.	n.d.	< LOD	< LOD	< LOD	n.d.
4-Nitrobenzoic acid	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD
Salicylic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	2.00	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	0.44	0.94	0.96	0.70	0.72	0.69
Nonenal	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.

Disinfection simulations

Table 37: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypochlorite by GC-MS and IC – parameter variation

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
THM									
Trichloromethane	7.12	8.03	15.67	2.26	8.03	21.09	1.67	8.03	14.31
Bromodichloromethane	6.28	10.76	10.48	1.43	10.76	10.82	2.47	10.76	17.09
Dibromochloromethane	2.87	5.12	11.16	2.52	5.12	4.75	0.80	5.12	9.62
Tribromomethane	0.95	1.19	28.99	7.17	1.19	2.66	1.52	1.19	1.95
I-THM									
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	0.31	0.27	n.d.	0.24
Bromochloroiodomethane	n.d.	n.d.	n.d.	0.23	n.d.	0.27	<LOD	n.d.	0.23
Dibromoiodomethane	n.d.	n.d.	1.40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	0.31	n.d.	n.d.	<LOD	<LOD	n.d.	<LOD
HNM									
Trichloronitromethane	0.82	0.99	1.45	n.d.	0.99	2.10	<LOD	0.99	0.75
Dibromonitromethane	n.d.	n.d.	<LOD	n.d.	n.d.	n.d.	<LOD	n.d.	n.d.
Bromonitromethane	2.70	2.93	6.36	1.04	2.93	2.10	0.80	2.93	3.26
HAL									
Trichloroacetaldehyde	6.77	8.62	5.30	n.d.	8.62	11.10	1.14	8.62	8.48

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
Tribromoacetaldehyde	1.32	1.12	5.14	n.d.	1.12	n.d.	2.60	1.12	n.d.
HAN									
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	0.92	0.94	1.45	<LOD	0.94	0.69	<LOD	0.94	0.44
Chloroacetonitrile	8.14	5.22	n.d.	n.d.	5.22	3.71	0.40	5.22	2.19
Dichloroacetonitrile	9.48	5.18	1.15	<LOD	5.18	4.16	0.43	5.18	2.52
Bromochloroacetonitrile	5.02	4.26	n.d.	0.61	4.26	2.88	1.40	4.26	1.99
Dibromoacetonitrile	2.45	2.70	12.05	1.77	2.70	3.00	0.69	2.70	1.31
Trichloroacetonitrile	3.15	1.69	n.d.	n.d.	1.69	1.73	0.51	1.69	1.03
HAM									
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK									
Trichloropropanone	1.29	0.81	0.61	n.d.	0.81	2.86	0.55	0.81	0.53
Dichloropropanone	9.03	5.86	n.d.	n.d.	5.86	11.9	8.22	5.86	5.99
Other									
Tetrachloromethane	0.89	0.78	0.77	n.d.	0.78	0.98	0.50	0.78	0.88
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	1.15	0.86	n.d.	0.52	0.86	0.64	0.38	0.86	0.61
Dibenzofuran	0.35	0.29	n.d.	<LOD	0.29	<LOD	0.31	0.29	<LOD

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
Oxohalides									
Chlorite	<LOD	0.22	<LOD	<LOD	0.22	0.22	<LOD	0.22	<LOD
Bromate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorate	7.2	5.9	34	1.8	5.9	6.5	8.2	5.9	11

Table 38: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypochlorite by LC-MS – parameter variation

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
HAA									
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	9.60	1.83	8.44	0.45	1.83	8.54	1.34	1.83	3.70
Trichloroacetic acid	7.07	12.1	9.85	4.47	12.1	19.4	10.6	12.1	7.69
Monobromoacetic acid	3.18	4.56	3.67	4.99	4.56	5.66	3.98	4.56	6.13
Dibromoacetic acid	1.81	0.84	5.10	0.66	0.84	1.10	0	0.84	2.32
Dibromochloroacetic acid	6.22	2.19	3.42	< LOD	2.19	5.92	0.93	2.19	2.71
Bromodichloroacetic acid	2.77	1.18	0.33	< LOD	1.18	4.93	0.81	1.18	2.56
Tribromoacetic acid	2.38	1.12	5.25	< LOD	1.12	1.46	0.41	1.12	0.38
Iodacetic acid	n.d.	n.d.	0.61	1.21	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	4.51	1.75	9.12	0.47	1.75	5.86	1.06	1.75	3.77
Other haloacids									

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
2,2-dichloropropanoic acid/Dalapon	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HBQ									
2,6-dichloro-1,4-benzoquinone	0.47	0.32	0.81	n.d.	0.32	< LOD	0.51	0.32	0.33
2,6-dibromo-1,4-benzoquinone	n.d.	< LOD	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD	0.52
Other halogenated									
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
Non halogenated									
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	n.d.	n.d.	< LOD	n.d.	< LOD	n.d.	n.d.	< LOD
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	0.94	15.2	1.15	0.94	5.43	1.68	0.94	4.43
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	0.25	13.5	n.d.	0.25	< LOD	0.21	0.25	0.77
Propanal	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	0.25
Benzaldehyde	n.d.	1.25	< LOD	0.23	1.25	1.46	0.86	1.25	0.96

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
Nonenal	n.d.	n.d.	n.d.	0.32	n.d.	n.d.	n.d.	n.d.	n.d.

Table 39: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypochlorite by GC-MS and IC – time variation

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
THM								
Trichloromethane	2.70	3.13	3.11	3.50	4.64	4.65	4.54	8.03
Bromodichloromethane	1.41	2.66	3.52	5.01	6.06	7.25	8.39	10.76
Dibromochloromethane	0.66	1.16	1.56	2.19	2.61	3.18	4.21	5.12
Tribromomethane	0.78	0.81	0.83	0.89	0.91	0.94	1.08	1.19
I-THM								
Dichloroiodomethane	n.d.	n.d.	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.41	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	0.31	0.26	0.26	0.26	0.24	0.21	<LOD	n.d.
HNM								
Trichloronitromethane	<LOD	0.57	<LOD	0.65	0.72	<LOD	<LOD	0.99
Dibromonitromethane	<LOD	<LOD	<LOD	n.d.	<LOD	<LOD	<LOD	n.d.
Bromonitromethane	<LOD	0.22	0.38	<LOD	0.26	0.38	0.27	2.93

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
HAL								
Trichloroacetaldehyde	2.39	1.87	1.76	2.11	2.61	2.39	5.06	8.62
Tribromoacetaldehyde	0.95	0.95	0.94	0.91	0.87	1.13	1.59	1.12
HAN								
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	0.23	0.23	0.28	0.31	0.27	0.33	0.39	0.94
Chloroacetonitrile	1.28	1.01	0.95	1.18	1.04	1.12	0.80	5.22
Dichloroacetonitrile	1.68	1.56	1.59	1.81	1.97	1.75	1.52	5.18
Bromochloroacetonitrile	1.59	1.75	1.96	2.13	2.26	2.72	3.06	4.26
Dibromoacetonitrile	1.23	1.79	1.76	1.97	1.80	2.28	3.41	2.70
Trichloroacetonitrile	0.35	0.32	0.26	0.36	0.41	0.45	0.27	1.69
HAM								
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK								
Trichloropropanon	1.12	1.05	0.89	0.96	1.19	1.11	0.73	0.81
Dichloropropanone	11.84	12.03	7.78	8.64	16.44	13.90	5.93	5.86
Other								
Tetrachloromethane	0.45	0.44	0.40	0.54	0.72	0.82	0.39	0.78
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	0.59	0.78	1.13	1.13	0.95	0.71	0.88	0.86

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Dibenzofuran	0.24	0.27	0.30	0.31	0.26	0.24	0.28	0.29
Oxohalides								
Chlorite	<LOD	n.m.	n.m.	<LOD	n.m.	n.m.	<LOD	<LOD
Bromate	<LOD	n.m.	n.m.	<LOD	n.m.	n.m.	<LOD	<LOD
Chlorate	6.3	n.m.	n.m.	6.3	n.m.	n.m.	6.4	5.8

24 h values taken from corresponding parameter variation experiment

Table 40: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypochlorite by LC-MS – time variation

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
HAA								
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	8.74	4.30	9.80	4.04	2.81	1.54	3.09	1.83
Trichloroacetic acid	8.97	12.5	12.5	13.2	14.5	15.9	17.5	12.1
Monobromoacetic acid	1.50	0.91	1.16	1.16	1.02	0.83	1.36	4.56
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.84
Dibromochloroacetic acid	1.25	1.17	2.63	2.62	2.85	1.22	3.98	2.19
Bromodichloroacetic acid	0.97	0.60	1.74	1.81	1.72	0.87	2.56	1.18
Tribromoacetic acid	< LOD	0.20	0.53	0.51	0.57	< LOD	0.68	1.12
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	1.77	0.45	1.63	1.84	1.91	0.85	2.21	1.75
Other haloacids								

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones								
2,6-dichloro-1,4-benzoquinone	< LOD	n.d.	< LOD	0.31	0.29	0.31	0.37	0.32
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.	< LOD	< LOD
Other halogenated								
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated								
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	n.d.	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.
Decanal	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	< LOD	1.33	1.33	1.33	0.92	1.79	0.94
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	< LOD	< LOD	1.74	1.98	1.78	< LOD	2.55	0.25
Propanal	n.d.	15.1	7.77	1.27	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	0.47	0.82	1.04	1.10	1.30	1.06	1.25
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

24 h values taken from corresponding parameter variation experiment

Table 41: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypobromite by GC-MS and IC – parameter variation

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOBr: 20 mg/L	NaOBr: 100mg/L	NaOBr: 200 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
THM									
Trichloromethane	0.62	0.60	0.59	1.28	1.60	2.17	0.69	0.60	0.57
Bromodichloromethane	0.70	0.69	0.68	n.d.	0.95	1.29	0.23	0.69	0.71
Dibromochloromethane	1.95	1.79	1.69	0.67	4.25	6.39	0.71	1.79	1.87
Tribromomethane	40.48	108.67	183.01	29.57	183.36	146.71	70.39	108.67	166.15
I-THM									
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HNM									
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	0.64	1.32	13.33	1.96	2.37	1.90	0.28	1.32	1.88
HAL									
Trichloroacetaldehyde	n.d.	n.d.	n.d.	n.d.	0.90	1.72	n.d.	n.d.	n.d.
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAN									

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOBr: 20 mg/L	NaOBr: 100mg/L	NaOBr: 200 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
Iodoacetonitrile	0.27	0.42	1.32	0.27	0.34	0.31	n.d.	0.42	n.d.
Bromoacetonitrile	1.32	5.13	26.18	0.29	2.12	1.29	<LOD	5.13	0.69
Chloroacetonitrile	n.d.	0.43	2.08	0.58	0.65	0.66	n.d.	0.43	0
Dichloroacetonitrile	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
Bromochloroacetonitrile	n.d.	n.d.	2.69	n.d.	n.d.	n.d.	<LOD	n.d.	n.d.
Dibromoacetonitrile	1.98	15.12	189.27	5.68	9.27	5.00	0.31	15.12	3.15
Trichloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAM									
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK									
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other									
Tetrachloromethane	0.63	0.62	0.62	n.d.	n.d.	n.d.	0.52	0.62	0.56
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	0.73	5.44	0.53	3.19	5.64	8.20	0.38	5.44	0.64
Dibenzofuran	0.26	0.18	0.19	0.32	0.46	0.69	0.32	0.18	0.15
Oxohalides									
Chlorite	8.8	5.8	3.0	0.16	11	24	<LOD	5.8	12

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOBr: 20 mg/L	NaOBr: 100mg/L	NaOBr: 200 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
Bromate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 42: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypobromite by LC-MS – parameter variation

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOBr: 20 mg/L	NaOBr: 100mg/L	NaOBr: 200 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
HAA									
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	88.1	181	2245	241	181	470	165	181	184
Dibromochloroacetic acid	< LOD	0.21	4.52	< LOD	0.21	< LOD	< LOD	0.21	n.d.
Bromodichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetic acid	47.8	145	3233	343	145	236	121	145	10.7
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	2.65	2.58	2.27	0.35	2.58	5.45	2.54	2.58	1.95
Other haloacids									
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of TOC			Variation of a.s.			Variation of temp.		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOBr: 20 mg/L	NaOBr: 100mg/L	NaOBr: 200 mg/L	T: 15 °C	T: 30 °C	T: 45 °C
Halobenzochinones									
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	< LOD	0.92	0.39	< LOD	n.d.	< LOD	< LOD	< LOD
Other halogenated									
2,6-dibromo-4-nitrophenol	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	0.27	n.d.	n.d.
2,4,6-tribromophenol	0.21	< LOD	0.45	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated									
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	n.d.	< LOD	< LOD	< LOD	< LOD	n.d.
Decanal	n.d.	< LOD	n.d.	0.45	< LOD	n.d.	n.d.	< LOD	n.d.
Acetaldehyde	n.d.	n.d.	0.58	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	< LOD	< LOD	< LOD	< LOD	n.d.	< LOD	< LOD	< LOD
Propanal	n.d.	11.1	1.88	3.90	11.1	n.d.	2.60	11.1	4.32
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 43: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypobromite by GC-MS – time variation

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
THM								
Trichloromethane	0.76	0.73	0.88	0.92	0.83	1.05	1.22	0.60
Bromodichloromethane	0.52	0.65	0.72	0.80	0.82	0.90	0.92	0.69
Dibromochloromethane	0.88	1.71	1.94	2.35	2.50	3.01	2.73	1.79
Tribromomethane	2.51	8.31	11.47	15.13	16.35	22.01	20.47	108.67
I-THM								
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.22	0.24	n.d.
HNM								
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00
Dibromonitromethane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d.
Bromonitromethane	n.d.	n.d.	0.37	0.53	0.70	1.02	1.16	1.32
HAL								
Trichloroacetaldehyde	n.d.	<LOQ	0.34	0.54	0.58	0.82	0.79	n.d.
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAN								
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.42

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Bromoacetonitrile	n.d.	<LOQ	<LOQ	<LOQ	0.23	0.36	0.31	5.13
Chloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.43
Dichloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ
Bromochloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetonitrile	0.46	0.57	0.81	1.02	1.12	1.46	1.40	15.12
Trichloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAM								
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK								
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other								
Tetrachloromethane	0.50	0.59	0.67	0.76	0.80	0.94	0.82	0.62
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	1.48	2.54	2.36	2.48	2.42	2.66	1.93	5.44
Dibenzofuran	0.22	0.40	0.39	0.36	0.23	0.39	0.31	0.18
Oxohalides								
Chlorite	n.d.	n.m.	n.m.	n.d.	n.m.	n.m.	n.d.	n.d.
Bromate	n.d.	n.m.	n.m.	n.d.	n.m.	n.m.	n.d.	n.d.
Chlorate	n.d.	n.m.	n.m.	n.d.	n.m.	n.m.	n.d.	n.d.

24 h values taken from corresponding parameter variation experiment

Table 44: Analysis of DBPs (in µg/L) after disinfection of artificial swimming pool water with sodium hypobromite by LC-MS – time variation

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
HAA								
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	1.12	11.0	12.8	13.5	13.9	16.4	17.1	181
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.21
Bromodichloroacetic acid	n.d.	n.d.	n.d.	1.87	n.d.	n.d.	n.d.	n.d.
Tribromoacetic acid	35.9	38.7	41.7	46.6	55.2	61.9	61.8	145
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.58
Other haloacids								
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones								
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
Other halogenated								
2,6-dibromo-4-nitrophenol	0.32	0.27	0.23	< LOD	< LOD	< LOD	< LOD	n.d.
2,4,6-tribromophenol	1.96	2.66	1.38	0.69	0.24	< LOD	n.d.	< LOD
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Non halogenated								
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Decanal	n.d.	n.d.	n.d.	n.d.	0.76	n.d.	1.23	< LOD
Acetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
Propanal	n.d.	n.d.	n.d.	n.d.	1.04	6.00	4.39	11.1
Benzaldehyde	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

24 h values taken from corresponding parameter variation experiment

Table 45: Analysis of DBPs (in µg/L) after disinfection of dissolved general matrix with sodium hypochlorite by GC-MS – parameter variation

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
THM											
Trichloromethane	5.47	25.53	105.69	23.23	25.53	27.36	15.32	25.53	43.42	3.36	42.02
Bromodichloromethane	0.69	3.71	0.66	1.01	3.71	1.05	1.92	3.71	0.94	0.78	0.88
Dibromochloromethane	n.d.	0.64	n.d.	n.d.	0.64	0.40	0.59	0.64	0.30	n.d.	n.d.

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
Tribromomethane	n.d.	0.84	n.d.	0.67	0.84	0.68	0.24	0.84	0.29	0.65	0.64
I-THM											
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HNM											
Trichloronitromethane	0.75	1.85	2.94	0.95	1.85	2.11	0.77	1.85	2.54	1.04	2.01
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	0.41	1.89	0.32	1.82	2.24	n.d.	n.d.	1.89	0.55	0.55	0.83
HAL											
Trichloroacetaldehyde	12.5	56.1	357	42.89	56.1	78.6	18.7	56.1	116	41.3	16.5
Tribromoacetaldehyde	0.95	1.59	0.74	0.84	1.59	1.76	n.d.	1.59	n.d.	n.d.	0.91
HAN											
Iodoacetonitrile	n.d.	n.d.	0.29	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	0.39	n.d.	n.d.	0.39	0.34	n.d.	0.39	0.48	n.d.	n.d.
Chloroacetonitrile	0.55	1.87	3.64	0.49	1.87	3.46	0.32	1.87	5.41	1.32	1.87
Dichloroacetonitrile	0.64	5.77	51.04	20.17	5.77	5.31	6.70	5.77	7.79	32.9	3.83
Bromochloroacetonitrile	0.27	2.38	0.32	0.92	2.38	2.10	0.31	2.38	2.14	1.60	1.01

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
Dibromoacetonitrile	n.d.	n.d.	n.d.	n.d.	1.36	1.28	n.d.	1.36	0.61	1.16	0.60
Trichloroacetonitrile	0.52	0.89	2.11	0.38	0.89	1.69	0.65	0.89	2.13	1.09	1.01
HAM											
Dichloroacetamide	0.00	n.d.	0.95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	0.32	n.d.	19.20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK											
Trichloropropanon	1.43	2.88	3.75	1.04	2.88	3.70	0.64	2.88	1.26	1.98	1.45
Dichloropropanone	3.12	5.58	2.66	2.17	5.58	27.36	3.98	5.58	7.21	4.09	6.63
Other											
Tetrachloromethane	0.51	1.35	2.62	0.37	1.35	2.51	1.25	1.35	0.78	1.06	1.50
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 46: Analysis of DBPs (in µg/L) after disinfection of dissolved general matrix with sodium hypochlorite by LC-MS – parameter variation

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
HAA											
Monochloroacetic acid	n.d.	15.3	n.d.	n.d.	15.3	12.5	2.67	15.3	36.9	8.35	7.85
Dichloroacetic acid	59.3	290	14.2	3.91	290	280	128	290	381	252	202

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
Trichloroacetic acid	66.7	328	2.73	1.95	328	159	161	328	323	275	236
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromodichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other haloacids											
2,2-dichloropropanoic acid/Dalapon	2.50	0.69	n.d.	n.d.	0.69	1.97	0.35	0.69	0.97	0.42	1.77
Halobenzochinones											
2,6-dichloro-1,4-benzoquinone	2.59	0.79	2.26	0.58	0.79	0.84	0.65	0.79	0.73	3.87	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated											
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	NaOCl: 10 mg/L	NaOCl: 50 mg/L	NaOCl: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated											
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	167	948	125	167	n.d.	0.29	167	200	174	145
Acetophenon	n.d.	n.d.	n.d.	0.58	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	0.58	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.
Propanal	n.d.	0.50	1.84	0.81	0.50	n.d.	n.d.	0.50	2.18	n.d.	0.75
Benzaldehyde	n.d.	17.5	6.07	5.85	17.5	n.d.	< LOD	17.5	20.9	5.85	35.1
Nonenal	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 47: Analysis of DBPs (in µg/L) after disinfection of dissolved general matrix with sodium hypochlorite by GC-MS – time variation

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
THM								
Trichloromethane	1.25	4.00	8.14	11.8	16.6	18.2	23.3	36.3

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Bromodichloromethane	0.71	0.76	0.81	0.81	0.70	0.84	0.82	1.9
Dibromochloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.66
Tribromomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
I-THM								
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HNM								
Trichloronitromethane	0.47	0.40	0.49	0.52	0.52	0.59	0.74	0.61
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	0.61	0.98	0.67	0.93	0.27	0.88	1.03	0.30
HAL								
Trichloroacetaldehyde	4.76	7.69	10.1	11.3	10.7	15.8	16.9	47.7
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAN								
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	0.74	0.81	0.95	0.94	0.65	0.91	0.95	0.73
Dichloroacetonitrile	1.80	6.07	10.2	11.6	11.6	11.1	8.962	1.528

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Bromochloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetonitrile	0.71	0.70	0.74	0.73	0.79	0.76	0.75	0.68
HAM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloropropanon	1.06	1.44	1.38	1.24	0.93	1.09	0.89	0.37
Dichloropropanone	8.32	4.72	5.98	6.70	7.47	10.3	7.24	7.25
Other	0.91	0.43	n.d.	n.d.	n.d.	n.d.	n.d.	0.69
Tetrachloromethane	1.87	2.00	2.22	2.32	2.36	2.48	2.46	2.15
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

24 h values taken from corresponding parameter variation experiment

Table 48: Analysis of DBPs (in µg/L) after disinfection of dissolved general matrix with sodium hypochlorite by LC-MS – time variation

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
HAA								
Monochloroacetic acid	0.54	1.04	1.90	2.96	1.94	2.78	3.40	15.3
Dichloroacetic acid	213	213	208	111	128	125	223	290

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Trichloroacetic acid	54.4	84.5	190	144	172	172	140	328
Monobromoacetic acid	0.51	0.48	0.67	0.60	0.28	n.d.	< LOD	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromodichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	0.30	0.26	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Other haloacids								
2,2-dichloropropanoic acid/Dalapon	0.91	0.43	< LOD	n.d.	n.d.	n.d.	n.d.	0.69
Halobenzochinones								
2,6-dichloro-1,4-benzoquinone	0.79	1.00	1.07	n.d.	n.d.	n.d.	n.d.	0.79
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated								
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated								
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	243	225	167
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.50
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	17.5
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

24 h values taken from corresponding parameter variation experiment

Table 49: Analysis of DBPs (in µg/L) after disinfection of dissolved general matrix with hydrogen peroxide by GC-MS – parameter variation

Substance	Variation of TOC		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L
THM			
Trichloromethane	n.d.	n.d.	n.d.
Bromodichloromethane	n.d.	n.d.	n.d.
Dibromochloromethane	n.d.	n.d.	n.d.
Tribromomethane	n.d.	n.d.	n.d.
I-THM			
Dichloroiodomethane	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.
HNM			
Trichloronitromethane	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.
HAL			
Trichloroacetaldehyde	n.d.	n.d.	n.d.
Tribromoacetaldehyde	n.d.	n.d.	n.d.
HAN			
Iodoacetonitrile	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.
Chloroacetonitrile	n.d.	n.d.	n.d.
Dichloroacetonitrile	n.d.	n.d.	n.d.
Bromochloroacetonitrile	n.d.	n.d.	n.d.
Dibromoacetonitrile	n.d.	n.d.	n.d.
Trichloroacetonitrile	n.d.	n.d.	n.d.
HAM			
Dichloroacetamide	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.
HK			
Trichloropropanon	n.d.	n.d.	n.d.
Dichloropropanone	n.d.	n.d.	n.d.

Substance	Variation of TOC		
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L
Other			
Tetrachloromethane	n.d.	n.d.	n.d.
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.

Table 50: Analysis of DBPs (in µg/L) after disinfection of dissolved general matrix with hydrogen peroxide by LC-MS – parameter variation

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	H2O2: 10 mg/L	H2O2: 50 mg/L	H2O2: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
HAA											
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	< LOD	< LOD	n.d.	< LOD	< LOD
Trichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromodichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other haloacids											
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones											
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of TOC			Variation of a.s.			Variation of temp.			Variation of pH	
	TOC: 0.1 mg/L	TOC: 1.0 mg/L	TOC: 10 mg/L	H2O2: 10 mg/L	H2O2: 50 mg/L	H2O2: 100 mg/L	T: 15 °C	T: 30 °C	T: 45 °C	pH 4	pH 9
Other halogenated											
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated											
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	1.31	22.3	n.d.	1.31	1.98	1.02	1.31	2.55	0.98	3.90
Acetophenon	n.d.	n.d.	n.d.	0.65	n.d.	< LOD	n.d.	n.d.	1.32	n.d.	< LOD
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	< LOD	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	< LOD	< LOD	< LOD
Propanal	1.15	2.00	2.50	3.82	2.00	2.01	2.35	2.00	1.05	1.28	0.71
Benzaldehyde	0.41	0.44	0.37	< LOD	0.44	0.56	0.24	0.44	0.76	< LOD	< LOD
Nonenal	< LOD	< LOD	< LOD	< LOD	< LOD	0.22	< LOD	< LOD	< LOD	< LOD	n.d.

Table 51: Analysis of DBPs (in µg/L) after disinfection of dissolved general matrix with hydrogen peroxide by LC-MS – time variation

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
HAA								
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	< LOD
Trichloroacetic acid	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Monobromoacetic acid	6.32	7.21	7.85	6.33	6.19	6.89	7.77	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromodichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other haloacids								
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones								
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated								
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of time							
	0 h	1 h	2 h	3 h	4 h	5 h	6 h	24 h
Non halogenated								
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	1.11	0.54	0.31	0.48	0.37	0.41	n.d.	1.31
Acetophenon	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	1.00	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	0.49	2.33	2.49	1.10	8.06	2.68	1.48	2.00
Benzaldehyde	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.44
Nonenal	< LOD	< LOD	n.d.	< LOD	n.d.	n.d.	< LOD	< LOD

24 h values taken from corresponding parameter variation experiment

Table 52: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with sodium hypochlorite by GC-MS and IC – parameter variation

Substance	Variation of TOC			Variation of a.s.		
	TOC: 2.5 µg/cm²	TOC: 25 µg/cm2	TOC: 80 µg/cm²	NaOCl: 0.5 g/L (0.05 %)	NaOCl: 5 g/L (0.5 %)	NaOCl: 10 g/L (1 %)
THM						
Trichloromethane	81.7	17.3	n.m.	n.d.	17.3	7.61
Bromodichloromethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Dibromochloromethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Tribromomethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
I-THM						
Dichloroiodomethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
HNM						
Trichloronitromethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
HAL						
Trichloroacetaldehyde	64.4	80.2	n.m.	4.96	80.2	12.4
Tribromoacetaldehyde	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
HAN						
Iodoacetonitrile	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Chloroacetonitrile	0.89	0.55	n.m.	n.d.	0.55	0.10
Dichloroacetonitrile	16.7	47.7	n.m.	0.07	47.7	1.05
Bromochloroacetonitrile	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Dibromoacetonitrile	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Trichloroacetonitrile	1.74	0.84	n.m.	n.d.	0.84	0.89
HAM						
Dichloroacetamide	n.d.	n.d.	n.m.	n.d.	n.d.	n.d.
Trichloroacetamide	1.30	n.d.	n.m.	n.d.	n.d.	n.d.
HK						
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of TOC			Variation of a.s.		
	TOC: 2.5 µg/cm²	TOC: 25 µg/cm2	TOC: 80 µg/cm²	NaOCl: 0.5 g/L (0.05 %)	NaOCl: 5 g/L (0.5 %)	NaOCl: 10 g/L (1 %)
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other						
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxohalides						
Chlorite	n.d.			n.d.	n.d.	n.d.
Bromate	0.64			0.46	n.d.	< LOD
Chlorate	13			24	13	1.1

Table 53: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with sodium hypochlorite by LC-MS – parameter variation

Substance	Variation of TOC			Variation of a.s.		
	TOC: 2.5 µg/cm2	TOC: 25 µg/cm2	TOC: 80 µg/cm2	NaOCl: 0.5 g/L (0.05%)	NaOCl: 5 g/L (0.5 %)	NaOCl: 10 g/L (1 %)
HAA						
Monochloroacetic acid	271	340	262	177	340	359
Dichloroacetic acid	213	234	238	19.6	234	307
Trichloroacetic acid	159	170	116	17.8	170	181
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromodichloroacetic acid	4.63	2.40	1.91	0.36	2.40	2.11
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	4.34	2.63	2.20	1.09	2.63	2.22
Other haloacids						
2,2-dichloropropanoic acid/Dalapon	634	743	563	< LOD	743	747
Halobenzochinones						
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of TOC			Variation of a.s.		
	TOC: 2.5 µg/cm2	TOC: 25 µg/cm2	TOC: 80 µg/cm2	NaOCl: 0.5 g/L (0.05%)	NaOCl: 5 g/L (0.5 %)	NaOCl: 10 g/L (1 %)
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated						
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Decanal	n.d.	n.d.	n.d.	2.78	n.d.	n.d.
Acetaldehyde	n.d.	n.d.	n.d.	20.1	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	n.d.	n.d.	n.d.	7.89	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	0.55	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 54: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with sodium hypochlorite by GC-MS and IC – time variation

Substance	Variation of time						
	0 min	20 min	40 min	60 min	80 min	100 min	120 min
THM							
Trichloromethane	11.81	27.4	23.3	21.4	11.1	20.4	20.8
Bromodichloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
I-THM							
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HNM							
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAL							
Trichloroacetaldehyde	9.45	62.4	65.1	58.9	57.2	70.9	67.4
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAN							
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of time						
	0 min	20 min	40 min	60 min	80 min	100 min	120 min
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	0.62	0.85	0.74	0.62	0.48	0.48	0.42
Dichloroacetonitrile	33.8	51.4	55.9	52.7	38.4	48.2	43.2
Bromochloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetonitrile	0.65	0.96	1.50	1.95	1.38	1.651	1.300
HAM							
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	1.21	3.92	4.59	3.88	2.36	2.57	2.81
HK							
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other							
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxohalides							
Chlorite	n.d.	n.d.	0.13	< LOD	n.d.	n.d.	0.13
Bromate	0.66	n.d.	0.14	0.16	0.66	0.01	0.14
Chlorate	11	11	11	11	11	11	11

120 min values taken from corresponding parameter variation experiment

Table 55: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with sodium hypochlorite by LC-MS – time variation

Substance	Variation of time						
	0 min	20 min	40 min	60 min	80 min	100 min	120 min
HAA							
Monochloroacetic acid	235	257	233	227	251	346	340
Dichloroacetic acid	191	237	225	233	239	297	234
Trichloroacetic acid	124	116	123	126	152	166	170
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromodichloroacetic acid	1.92	1.91	2.17	2.16	1.92	2.66	2.40
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	1.65	1.84	2.54	2.55	2.23	2.95	2.63
Other haloacids							
2,2-dichloropropanoic acid/Dalapon	696	602	542	649	646	791	743
Halobenzochinones							
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated							
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of time						
	0 min	20 min	40 min	60 min	80 min	100 min	120 min
Non halogenated							
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

120 min values taken from corresponding parameter variation experiment

Table 56: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with chloramine T by GC-MS – parameter variation

Substance	Variation of TOC		Variation of a.s.		
	TOC: 2.5 µg/cm²	TOC: 25 µg/cm²	Chloramine T: 2.5 g/L (0.25 %)	Chloramine T: 25 g/L (2.5 %)	Chloramine T: 50 g/L (5 %)
THM					
Trichloromethane	1.36	0.31	n.d.	0.31	n.d.
Bromodichloromethane	0.52	0.50	0.48	0.50	0.52
Dibromochloromethane	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromomethane	n.d.	n.d.	n.d.	n.d.	n.d.
I-THM					
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.
HNM					
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.
HAL					
Trichloroacetaldehyde	259	262	31.9	262	31.1
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.
HAN					
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetonitrile	6.05	2.86	n.d.	2.86	0.73
Bromochloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetonitrile	0.64	0.61	n.d.	0.61	0.60
HAM					
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	2.28	1.89	n.d.	1.89	n.d.
HK					
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	5.0

Substance	Variation of TOC		Variation of a.s.		
	TOC: 2.5 µg/cm²	TOC: 25 µg/cm²	Chloramine T: 2.5 g/L (0.25 %)	Chloramine T: 25 g/L (2.5 %)	Chloramine T: 50 g/L (5 %)
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.
Other					
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.
Oxohalides					
Chlorite	n.d.	n.m.	n.d.	n.d.	n.d.
Bromate	n.d.	n.m.	n.d.	n.d.	n.d.
Chlorate	n.d.	n.m.	n.d.	n.d.	n.d.

Table 57: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with chloramine T by LC-MS – parameter variation

Substance	Variation of TOC			Variation of a.s.		
	TOC: 2.5 µg/cm²	TOC: 25 µg/cm²	TOC: 80 µg/cm²	Chloramine T: 2.5 g/L (0.25 %)	Chloramine T: 25 g/L (2.5 %)	Chloramine T: 50 g/L (5 %)
HAA						
Monochloroacetic acid	6.44	9.49	17.6	8.98	9.49	5.87
Dichloroacetic acid	15.8	20.5	448	9.79	20.5	16.3
Trichloroacetic acid	8.53	8.14	20.2	4.43	8.14	8.39
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	0.36	0.39	0.37	n.d.	0.39	n.d.
Bromodichloroacetic acid	0.52	0.59	0.55	0.46	0.59	0.59
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	0.63	0.62	1.40	0.56	0.62	0.86
Other haloacids						
2,2-dichloropropanoic acid/Dalapon	0.26	0.35	0.42	0.21	0.35	0.31
Halobenzochinones						
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	2.14	n.d.	n.d.	n.d.

Substance	Variation of TOC			Variation of a.s.		
	TOC: 2.5 µg/cm²	TOC: 25 µg/cm²	TOC: 80 µg/cm²	Chloramine T: 2.5 g/L (0.25 %)	Chloramine T: 25 g/L (2.5 %)	Chloramine T: 50 g/L (5 %)
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated						
Phthalimide	< LOD	< LOD	< LOD	n.d.	< LOD	< LOD
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	< LOD	n.d.	n.d.	< LOD	n.d.	n.d.
Propanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 58: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with chloramine T by GC-MS – time variation

Substance	Variation of time						
	0 min	20 min	40 min	60 min	80 min	100 min	120 min
THM							
Trichloromethane	n.d.	n.d.	0.49	0.37	1.57	0.29	1.73
Bromodichloromethane	0.50	0.49	0.51	0.51	0.50	0.49	0.50
Dibromochloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
I-THM							
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HNM							
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAL							
Trichloroacetaldehyde	1.30	86.7	149	172	193	201	228
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAN							
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of time						
	0 min	20 min	40 min	60 min	80 min	100 min	120 min
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetonitrile	n.d.	1.01	2.39	2.92	3.21	2.69	3.52
Bromochloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetonitrile	n.d.	0.59	0.60	0.60	0.60	0.60	0.61
HAM							
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	0.74	1.27	1.46	1.47	1.50	1.56
HK							
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other							
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxohalides							
Chlorite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chlorate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

120 min values taken from corresponding parameter variation experiment

Table 59: Analysis of DBPs (in µg/L) after disinfection of general matrix on hard surface with chloramine T by LC-MS – time variation

Substance	Variation of time						
	0 min	20 min	40 min	60 min	80 min	100 min	120 min
HAA							
Monochloroacetic acid	5.71	9.30	164	21.3	6.95	7.01	9.49
Dichloroacetic acid	12.1	40.3	1247	618	15.0	14.5	20.5
Trichloroacetic acid	5.91	15.4	53.9	35.9	5.73	8.05	8.14
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	n.d.	0.57	0.46	0.83	< LOD	0.59	0.39
Bromodichloroacetic acid	0.23	0.36	0.97	0.73	0.20	0.32	0.59
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	0.48	0.47	2.09	2.50	0.49	0.43	0.62
Other haloacids							
2,2-dichloropropanoic acid/Dalapon	0.28	0.29	0.26	0.25	0.29	0.24	0.35
Halobenzochinones							
2,6-dichloro-1,4-benzoquinone	n.d.	n.d.	4.57	4.82	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated							
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Variation of time						
Non halogenated							
Phthalimide	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Decanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	< LOD	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.
Salicylic acid	< LOD	n.d.	n.d.	n.d.	< LOD	< LOD	n.d.
Propanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

120 min values taken from corresponding parameter variation experiment

Genuine disinfection samples

Table 60: Analysis of DBPs in swimming pools by GC-MS

Substance	Open air swimming pools			
	Non-swimmers pool [µg/L]	Children's pool [µg/L]	Swimming pool [µg/L]	Fill-up water [µg/L]
THM				
Trichloromethane	3.42	4.27	7.49	6.50
Bromodichloromethane	0.40	0.50	0.96	0.91
Dibromochloromethane	0.17	0.18	0.21	0.20
Tribromomethane	0.11	0.10	0.10	0.10
I-THM				
Dichloroiodomethane	n.d.	1.38	n.d.	0.98
Bromochloroiodomethane	n.d.	0.14	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.
HNM				
Trichloronitromethane	0.36	0.45	0.53	0.47
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.	n.d.
HAL				
Trichloroacetaldehyde	17.2	19.9	17.1	24.4
Tribromoacetaldehyde	0.60	0.65	0.74	0.70
HAN				
Iodoacetonitrile	n.d.	0.29	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	n.d.	n.d.	<LOD	<LOD
Dichloroacetonitrile	2.84	3.42	4.63	3.94
Bromochloroacetonitrile	0.84	0.95	1.63	1.09
Dibromoacetonitrile	n.d.	0.17	0.18	0.17
Trichloroacetonitrile	0.50	0.50	0.50	0.51
HAM				
Dichloroacetamide	3.75	3.76	2.73	4.52
Trichloroacetamide	0.68	0.80	0.64	0.89

Substance	Open air swimming pools			
	Non-swimmers pool [µg/L]	Children's pool [µg/L]	Swimming pool [µg/L]	Fill-up water [µg/L]
HK				
Trichloropropanon	7.39	7.97	9.87	9.74
Dichloropropanone	0.49	0.49	0.49	0.50
Other halogenated				
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.
1.2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.
Other non-halogenated				
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.

Table 61: Analysis of DBPs in swimming pools by LC-MS

Substance	Open air swimming pools			
	Non-swimmers pool [µg/L]	Children's pool [µg/L]	Swimming pool [µg/L]	Fill-up water [µg/L]
HAA				
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	18.1	17.8	13.5	18.2
Trichloroacetic acid	55.8	58.6	76.1	53.9
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	0.31	0.21	0.29	0.32
Bromodichloroacetic acid	2.95	2.84	2.98	2.96
Tribromoacetic acid	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	1.16	0.90	0.78	1.01
Other haloacids				
2,2-dichloropropanoic acid/Dalapon	3.79	3.82	2.57	3.80
Halobenzochinones				
2,6-dichloro-1.4-benzoquinone	0.51	< LOD	< LOD	< LOD
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.
Other halogenated				

Substance	Open air swimming pools			
	Non-swimmers pool [µg/L]	Children's pool [µg/L]	Swimming pool [µg/L]	Fill-up water [µg/L]
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.
Non halogenated				
Phthalimide	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.
Benzophenone	n.d.	n.d.	n.d.	n.d.
Decanal	4.98	5.39	5.21	4.92
Acetaldehyde	14.4	13.4	10.7	14.7
Acetophenon	1.33	1.20	4.67	6.60
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.
Salicylic acid	< LOD	n.d.	1.17	0.41
Propanal	2.58	2.63	3.71	4.23
Benzaldehyde	0.27	0.21	0.53	0.41
Nonenal	0.43	< LOD	< LOD	< LOD

Table 62: Analysis of DBPs in spas by GC-MS

Substance	Thermal spa pools							
	Fill-up water [µg/L]	Hot water pool [µg/L]	Sauna pool [µg/L]	Main pool [µg/L]	Sitting pool [µg/L]	Hamam [µg/L]	Cold water pool [µg/L]	Whirl pool [µg/L]
THM								
Trichloromethane	2.89	4.06	4.12	6.90	8.41	20.89	53.36	5.13
Bromodichloromethane	0.64	5.35	3.20	12.8	15.9	6.20	22.4	5.70
Dibromochloromethane	0.65	17.9	27.9	31.8	36.2	2.59	11.6	25.0
Tribromomethane	2.81	52.1	238.35	29.17	39.65	2.78	4.22	74.2
I-THM								
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	0.23	0.68	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.31	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	0.81	0.66	n.d.	n.d.	0.36	0.23	0.22
HNM								
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	0.99	2.74	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	0.10	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	2.52	2.40	7.50	1.68	n.d.	n.d.	13.93
HAL								
Trichloroacetaldehyde	n.d.	0.00	0	1.63	0.58	3.00	20.4	1.63
Tribromoacetaldehyde	n.d.	6.83	9.30	3.75	4.24	0	0.00	30.9
HAN								

Substance	Thermal spa pools							
	Fill-up water [µg/L]	Hot water pool [µg/L]	Sauna pool [µg/L]	Main pool [µg/L]	Sitting pool [µg/L]	Hamam [µg/L]	Cold water pool [µg/L]	Whirl pool [µg/L]
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	n.d.	n.d.	0.71	n.d.	n.d.	n.d.	0.89	1.69
Dichloroacetonitrile	n.d.	0.79	0.46	2.92	2.02	1.32	6.95	4.06
Bromochloroacetonitrile	n.d.	6.05	8.32	10.6	8.65	0.88	4.84	27.1
Dibromoacetonitrile	n.d.	28.8	103	21.7	20.6	0.92	3.67	151
Trichloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAM								
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK								
Trichloropropanon	n.d.	n.d.	n.d.	1.27	1.16	4.77	11.2	n.d.
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated								
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1.2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 63: Analysis of DBPs in spas by LC-MS

Substance	Thermal spa pools							
	Fill-up water [µg/L]	Hot water pool [µg/L]	Sauna pool [µg/L]	Main pool [µg/L]	Sitting pool [µg/L]	Hamam [µg/L]	Cold water pool [µg/L]	Whirl pool [µg/L]
HAA								
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	1.79	0.95	1.20	1.45	1.45	5.03	2.35	3.07
Trichloroacetic acid	0.52	n.d.	n.d.	4.43	1.96	16.9	16.50	6.86
Monobromoacetic acid	n.d.	n.d.	1.00	n.d.	n.d.	n.d.	n.d.	2.68
Dibromoacetic acid	n.d.	4.72	35.66	5.15	4.19	n.d.	n.d.	42.6
Dibromochloroacetic acid	n.d.	4.41	23.8	21.6	22.8	0.59	2.33	34.8
Bromodichloroacetic acid	n.d.	1.87	2.30	7.54	7.43	2.03	3.53	7.68
Tribromoacetic acid	< LOD	3.15	16.1	2.83	2.72	n.d.	n.d.	9.56
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	n.d.	0.41	2.74	2.02	1.48	0.81	0.58	10.4
Other haloacids								
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	0.88	1.23	1.92	2.06	n.d.
Halobenzochinones								
2,6-dichloro-1.4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated								
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Substance	Thermal spa pools							
	Fill-up water [µg/L]	Hot water pool [µg/L]	Sauna pool [µg/L]	Main pool [µg/L]	Sitting pool [µg/L]	Hamam [µg/L]	Cold water pool [µg/L]	Whirl pool [µg/L]
2,4,6-tribromophenol	0.15	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.32
3-bromo-5-chloro-4-hydroxybenzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	< LOD	n.d.
Non halogenated								
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzophenone	< LOD	< LOD	< LOD	0.22	< LOD	< LOD	0.27	0.47
Decanal	n.d.	n.d.	0.70	0.61	n.d.	< LOD	n.d.	n.d.
Acetaldehyde	n.d.	5.39	10.8	7.45	6.96	0.53	3.96	19.6
Acetophenon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	n.d.	0.22	0.18	n.d.	0.24	n.d.
Propanal	0.36	0.49	1.50	1.18	n.d.	1.31	n.d.	1.07
Benzaldehyde	n.d.	n.d.	0.64	0.61	n.d.	n.d.	n.d.	1.78
Nonenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 64: Analysis of DBPs in industrial cooling systems F21, KKA1 and RKW SM by GC-MS and IC (oxohalides)

System code:	F21		KKA1		RKW SM	
	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]
THM						

System code:	F21		KKA1		RKW SM	
	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]
Trichloromethane	0.30	1.92	0.00	0.00	0.00	6.90
Bromodichloromethane	0.78	0.60	0.52	0.99	0.78	12.76
Dibromochloromethane	0.44	0.31	0.29	2.67	1.34	31.75
Tribromomethane	0.00	0.00	0.00	9.08	4.53	29.17
I-THM						
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HNM						
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAL						
Trichloroacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAN						
Iodoacetonitrile	0.52	n.d.	n.d.	0.25	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.	23.3	n.d.	n.d.

System code:	F21		KKA1		RKW SM	
	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]
Chloroacetonitrile	n.d.	n.d.	n.d.	1.19	n.d.	n.d.
Dichloroacetonitrile	n.d.	n.d.	n.d.	17.5	n.d.	n.d.
Bromochloroacetonitrile	n.d.	n.d.	n.d.	3.74	n.d.	n.d.
Dibromoacetonitrile	0.76	n.d.	n.d.	10.3	n.d.	n.d.
Trichloroacetonitrile	4.55	n.d.	n.d.	n.d.	n.d.	n.d.
HAM						
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK						
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other						
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1.2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxohalides						
Chlorite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chlorate	0.83	3.05	n.d.	5.63	n.d.	2.35

Table 65: Analysis of DBPs in industrial cooling systems HoA, SpW and Ko by GC-MS and IC (oxohalides)

System code:	HoA	SpW				Ko			
	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water SpW1/2 [µg/L]	Cooling water SpW3 [µg/L]	Cooling water SpW4 [µg/L]	Cooling water Ko 1 [µg/L]	Cooling water Ko 2 [µg/L]	Cooling water Ko 3 [µg/L]	Cooling water Ko 4 [µg/L]
THM									
Trichloromethane	13.2	n.d.	n.d.	n.d.	n.d.	17.1	50.1	4.52	4.48
Bromodichloromethane	13.05	0.90	0.52	0.50	0.54	0.63	0.73	0.51	0.51
Dibromochloromethane	8.50	1.44	0.31	0.28	0.29	0.28	0.27	0.27	0.28
Tribromomethane	1.52	4.88	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
I-THM									
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	1.03	1.14	1.25	1.23
HNM									
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAL									
Trichloroacetaldehyde	11.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

System code:	HoA	SpW				Ko			
	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water SpW1/2 [µg/L]	Cooling water SpW3 [µg/L]	Cooling water SpW4 [µg/L]	Cooling water Ko 1 [µg/L]	Cooling water Ko 2 [µg/L]	Cooling water Ko 3 [µg/L]	Cooling water Ko 4 [µg/L]
HAN									
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetonitrile	1.34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetonitrile	1.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetonitrile	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAM									
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK									
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other									
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1.2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

System code:	HoA	SpW				Ko			
	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water SpW1/2 [µg/L]	Cooling water SpW3 [µg/L]	Cooling water SpW4 [µg/L]	Cooling water Ko 1 [µg/L]	Cooling water Ko 2 [µg/L]	Cooling water Ko 3 [µg/L]	Cooling water Ko 4 [µg/L]
Oxohalides									
Chlorite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chlorate	0.23	0.59	0.86	0.75	2.28	0.98	3.37	2.89	1.42

Table 66: Analysis of DBPs in industrial cooling systems KKW, StGas, MKW and ML by GC-MS and IC (oxohalides)

System code:	KKW		StGas	MKW	ML	
	Fill-up water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water ML 1 [µg/L]	Cooling water ML 2 [µg/L]
THM						
Trichloromethane	n.d.	n.d.	n.d.	n.d.	91.3	233
Bromodichloromethane	0.50	0.49	0.48	0.49	3.77	1.88
Dibromochloromethane	0.32	0.26	0.26	0.26	0.79	0.74
Tribromomethane	n.d.	n.d.	n.d.	n.d.	0.98	1.69
I-THM						
Dichloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Triiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroiodomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

System code:	KKW		StGas	MKW	ML	
	Fill-up water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water ML 1 [µg/L]	Cooling water ML 2 [µg/L]
HNM						
Trichloronitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromonitromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAL						
Trichloroacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tribromoacetaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAN						
Iodoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HAM						
Dichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trichloroacetamide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HK						
Trichloropropanon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

System code:	KKW		StGas	MKW	ML	
	Fill-up water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water ML 1 [µg/L]	Cooling water ML 2 [µg/L]
Dichloropropanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other						
Tetrachloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1.2-Dibromo-3-chloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methylnaphtalin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxohalides						
Chlorite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chlorate	0.55	n.d.	0.14	n.d.	n.d.	n.d.

Table 67: Analysis of DBPs in industrial cooling systems F21, KKA1 and RKW SM by LC-MS

System code:	F21		KKA1		RKW SM	
	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]
HAA						
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	0.40	n.d.	0.24	18.9	n.d.	n.d.
Trichloroacetic acid	1.07	1.08	0.24	12.4	0	0.50
Monobromoacetic acid	0.24	n.d.	0.35	2.56	0.20	0.22

System code:	F21		KKA1		RKW SM	
	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]
Dibromoacetic acid	n.d.	n.d.	n.d.	124	n.d.	n.d.
Dibromochloroacetic acid	< LOD	< LOD	0.24	7.07	< LOD	0.47
Bromodichloroacetic acid	n.d.	2.36	n.d.	5.18	n.d.	n.d.
Tribromoacetic acid	n.d.	n.d.	< LOD	39.0	0.34	1.10
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	n.d.	n.d.	n.d.	27.50	n.d.	n.d.
Other haloacids						
2,2-dichloropropanoic acid/Dalapon	0.29	0.66	n.d.	n.d.	n.d.	n.d.
Halobenzochinones						
2,6-dichloro-1.4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						
2,6-dibromo-4-nitrophenol	< LOD	n.d.	n.d.	0.77	n.d.	0.64
2,4,6-tribromophenol	< LOD	< LOD	0	0.67	< LOD	0.33
3-bromo-5-chloro-4-hydroxybenzaldehyde	0.52	0.25	< LOD	< LOD	0.23	< LOD
Non halogenated						
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.
Benzophenone	< LOD	< LOD	< LOD	< LOD	n.d.	< LOD

System code:	F21		KKA1		RKW SM	
	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water [µg/L]
Decanal	0.76	0.95	0.69	0.51	0.83	0.93
Acetaldehyde	4.55	5.27	6.16	4.53	63.6	1.36
Acetophenon	2.16	2.29	1.57	1.71	2.35	0.40
4-Nitrobenzoic acid	< LOD	0.20	< LOD	< LOD	n.d.	< LOD
Salicylic acid	0.41	n.d.	n.d.	n.d.	n.d.	n.d.
Propanal	5.19	3.39	1.33	9.53	11.0	3.43
Benzaldehyde	0.52	0.25	< LOD	n.d.	n.d.	n.d.
Nonenal	n.d.	n.d.	n.d.	0.35	n.d.	n.d.

Table 68: Analysis of DBPs in industrial cooling systems HoA, SpW and Ko by LC-MS

System code	HoA	SpW				Ko			
	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water SpW1/2 [µg/L]	Cooling water SpW3 [µg/L]	Cooling water SpW4 [µg/L]	Cooling water Ko 1 [µg/L]	Cooling water Ko 2 [µg/L]	Cooling water Ko 3 [µg/L]	Cooling water Ko 4 [µg/L]
HAA									
Monochloroacetic acid	1.13	< LOD	1.67	n.d.	0.36	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	11.3	0.36	0.79	0.54	0.87	3.21	8.80	4.86	2.20
Trichloroacetic acid	1.76	n.d.	n.d.	n.d.	0.21	1.84	n.d.	0.82	3.28
Monobromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	4.77	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibromochloroacetic acid	2.52	n.d.	0.20	n.d.	0.26	n.d.	n.d.	n.d.	n.d.

System code	HoA	SpW				Ko			
	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water SpW1/2 [µg/L]	Cooling water SpW3 [µg/L]	Cooling water SpW4 [µg/L]	Cooling water Ko 1 [µg/L]	Cooling water Ko 2 [µg/L]	Cooling water Ko 3 [µg/L]	Cooling water Ko 4 [µg/L]
Bromodichloroacetic acid	3.05	n.d.	n.d.	n.d.	n.d.	< LOD	0.39	0.33	0.26
Tribromoacetic acid	1.71	0.51	0.28	n.d.	0.26	< LOD	< LOD	< LOD	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	6.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
Other haloacids									
2,2-dichloropropanoic acid/Dalapon	0.21	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
Halobenzochinones									
2,6-dichloro-1.4-benzoquinone	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated									
2,6-dibromo-4-nitrophenol	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	< LOD	0.27	n.d.	n.d.	< LOD	< LOD	n.d.	n.d.	n.d.
Non halogenated									
Phthalimide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-cyclohexyl-2-pyrrolidone	n.d.	n.d.	n.d.	n.d.	n.d.	0.20	< LOD	< LOD	0.20

System code	HoA	SpW				Ko			
	Cooling water [µg/L]	Fill-up water [µg/L]	Cooling water SpW1/2 [µg/L]	Cooling water SpW3 [µg/L]	Cooling water SpW4 [µg/L]	Cooling water Ko 1 [µg/L]	Cooling water Ko 2 [µg/L]	Cooling water Ko 3 [µg/L]	Cooling water Ko 4 [µg/L]
Benzophenone	n.d.	n.d.	n.d.	n.d.	0.22	n.d.	n.d.	n.d.	n.d.
Decanal	< LOD	0.39	0.21	n.d.	n.d.	0.44	0.73	0.22	1.04
Acetaldehyde	3.47	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenon	0.48	0.42	0.68	0.60	0.45	0.57	0.37	n.d.	0.68
4-Nitrobenzoic acid	< LOD	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	n.d.	n.d.	0.59	n.d.	n.d.	0.90	n.d.	n.d.
Propanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	0.26	n.d.	n.d.	n.d.	n.d.	0.22	< LOD	< LOD	< LOD
Nonenal	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	< LOD	n.d.

Table 69: Analysis of DBPs in industrial cooling systems KKW, StGas, MKW and ML by LC-MS

System code	KKW		StGas	MKW	ML	
	Fill-up water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water ML 1 [µg/L]	Cooling water ML 2 [µg/L]
HAA						
Monochloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dichloroacetic acid	0.65	n.d.	n.d.	n.d.	15.9	4.46
Trichloroacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Monobromoacetic acid	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
Dibromoacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

System code	KKW		StGas	MKW	ML	
	Fill-up water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water ML 1 [µg/L]	Cooling water ML 2 [µg/L]
Dibromochloroacetic acid	n.d.	n.d.	< LOD	< LOD	n.d.	n.d.
Bromodichloroacetic acid	n.d.	0.24	n.d.	0.31	0.37	0.28
Tribromoacetic acid	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
Iodacetic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromochloroacetic acid	< LOD	n.d.	n.d.	n.d.	0.66	< LOD
Other haloacids						
2,2-dichloropropanoic acid/Dalapon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halobenzochinones						
2,6-dichloro-1.4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-dibromo-1,4-benzoquinone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other halogenated						
2,6-dibromo-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-tribromophenol	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
3-bromo-5-chloro-4-hydroxybenzaldehyde	0.21	n.d.	n.d.	n.d.	n.d.	n.d.
Non halogenated						
Phthalimide	n.d.	n.d.	< LOD	< LOD	< LOD	0.20
N-cyclohexyl-2-pyrrolidone	n.d.	< LOD	< LOD	n.d.	n.d.	n.d.
Benzophenone	n.d.	< LOD	< LOD	n.d.	< LOD	n.d.
Decanal	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.

System code	KKW		StGas	MKW	ML	
	Fill-up water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water [µg/L]	Cooling water ML 1 [µg/L]	Cooling water ML 2 [µg/L]
Acetaldehyde	n.d.	1.58	2.43	n.d.	n.d.	2131
Acetophenon	< LOD	n.d.	< LOD	n.d.	n.d.	n.d.
4-Nitrobenzoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Salicylic acid	n.d.	< LOD	< LOD	n.d.	4.96	10.8
Propanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nonenal	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD