ECHA
EUROPEAN CHEMICALS AGENCY

GUIDANCE

# Guidance on the Biocidal Products Regulation

## Volume V, Guidance on Disinfection By-Products

Version 1.0
January 2017

# LEGAL NOTICE

This document aims to assist users in complying with their obligations under the Biocidal Products Regulation (BPR). However, users are reminded that the text of the BPR is the only authentic legal reference and that the information in this document does not constitute legal advice. Usage of the information remains under the sole responsibility of the user. The European Chemicals Agency does not accept any liability with regard to the use that may be made of the information contained in this document.

**Guidance on the BPR: Guidance on Disinfection By-Products**

**Reference:** ECHA-17-G-01-EN
**Cat.Number:** ED-02-17-037-EN-N
**ISBN:** 978-92-9495-732-0
**DOI:** 10.2823/72847

**Publ.date:** January 2017
**Language:** EN

© European Chemicals Agency, 2017

If you have questions or comments in relation to this document please send them (indicating the document reference, issue date, chapter and/or page of the document which your comment refers) using the Guidance feedback form. The feedback form can be accessed via the ECHA website or directly via the following link:
https://comments.echa.europa.eu/comments_cms/FeedbackGuidance.aspx

**European Chemicals Agency**

Mailing address: P.O. Box 400, FI-00121 Helsinki, Finland
Visiting address: Annankatu 18, Helsinki, Finland

# DOCUMENT HISTORY

| Version | Comment | Date |
|---|---|---|
| Version 1.0 | First edition | January 2017 |

# PREFACE

This document describes the BPR obligations and how to fulfil them.

The application of halogen-containing biocides leads to the formation of disinfection by-products (DBPs). These DBPs have been shown to include hazardous substances that may pose a risk to human health or the environment. The Competent Authorities (CAs) and the Technical Meetings (TM) decided that a risk assessment of DBPs should be conducted as part of the authorisation of the halogenated biocidal products. The TM agreed that a harmonised approach to such a risk assessment should be found for all halogenated disinfectants at the stage of for Annex I inclusion (of the then BPD 98/8/EC, now active substance approval for Biocidal Products Regulation (BPR)) instead of postponing it to the national authorisation stage.

From 2011 onwards the Netherlands has done work to develop such a harmonised approach for both the human health risk assessment and environmental risk assessment of DBPs. Several member states (MS) have participated in this process and given their input.

An initial document was presented at TMIV-2011. The main conclusion was that there were insufficient data available in the dossiers to assess the risks of DBPs following human exposure and environmental exposure. Where possible, identification of the DBPs formed and a qualitative assessment of those DBPs should be included in the Competent Authority Reports (CARs).

Regarding **human health risk assessment**, as decided at the CA and (former) TM-level, priority was given to PT2 (swimming-water) since this is considered as the most relevant from the point of human exposure to DBPs and its associated possible risk to health. The starting point of the human health risk assessment for DBPs was the decision by the CA-meeting to use existing national limits for individual (groups of) DBPs in swimming- and/or drinking-water. This was agreed to by TMII-2012 as being the appropriate first tier in the human health risk evaluation for DBPs. Based on that decision proposals for a pragmatic approach were developed. Prior to TM II-2012 these proposals were circulated amongst, a number of whom gave written input. At the TM III-2012 formal agreement was obtained on the various points raised in these proposals. In a subsequent document NL outlined what could be the way forward as to the actual application of the method for the envisaged human health risk assessment.

Regarding **environmental risk assessment**, it was further agreed that discussion papers from the workshop on Ballast Water Treatment should be taken into account, together with the input from other MS and industry (IND). A revised document, first presented at TMI-2012, incorporated a more in-depth analysis of the relevance of (groups) of DBPs and provided further information required for the assessment. On special request from the European Commission (COM), the document investigated in particular whether the strategy and/or the conclusions of the EU Risk Assessment Report (EU-RAR) of sodium hypochlorite under the former Existing Substances Regulation (793/93/EEC)[1] could be taken over for biocide risk assessment. The document summarised the information on DBP-formation and risk assessment focusing on the following product types (PTs): PT2 (waste water treatment), PT11 (cooling water), and PT12 (pulp and paper) and was discussed again at TMII-2012. At TMIII-2012, NL

[1] EC. 2007. European Union Risk Assessment Report SODIUM HYPOCHLORITE, CAS No: 7681-52-9, EINECS No: 231-668-3, Final report, November 2007. Rapporteur Member State Italy, http://esis.jrc.ec.europa.eu/doc/existing-chemicals/risk_assessment/REPORT/sodiumhypochloritereport045.pdf.

presented a combined document including both the human and environmental risk assessment in order to update the discussions and to integrate the various documents that had been presented at earlier TMs. The main problem identified at that stage was the lack of adequate monitoring data.

The document was then presented to the CA-meeting in December 2012 and March 2013 with a request to decide on the timelines and responsibilities for further action. No agreement was reached during those CA-meetings and the subject was put on hold.

After the Biocides Product Regulation (BPR, Regulation (EU) 528/2012) came into force and the biocides assessment had moved to the European Chemicals Agency (ECHA), an Ad Hoc Working Group for disinfectant by-products (ad hoc DBP WG) was established under the Biocides Product Committee (BPC) to re-activate the process and finalise the guidance. Under the mandate of this ad hoc DBP WG, the Netherlands organised a workshop, which was held on June 25 2015 in Amsterdam. The goal of this workshop was to settle all outstanding issues and to allow finalising the description of the methods for the human health and environmental risk assessment of DBPs.

Based on the workshop discussions, the present document provides a strategy for the human health risk assessment and the environmental risk assessment of DBPs. With this document the responsible parties for risk assessment of halogenated disinfectants can start the work on the evaluation of DBPs.

### Applicability of Guidance

Guidance on applicability of new guidance or guidance related documents for active substance approval is given in the published document "*Applicability time of new guidance and guidance-related documents in active substance approval*" available on the BPC Webpage[2] [https://echa.europa.eu/about-us/who-we-are/biocidal-products-committee] and for applicability of guidance for product authorisation, please see the CA-document CA-july2012-doc6.2d (final), available on the ECHA Guidance page [CA-July2012-doc6.2d(final)].

[2] Link available under Working Procedures (right column) [https://echa.europa.eu/about-us/who-we-are/biocidal-products-committee]

# Table of Contents

LEGAL NOTICE ..... 2
DOCUMENT HISTORY ..... 3
PREFACE ..... 4
LIST OF ABBREVIATIONS ..... 9
1. GENERAL INTRODUCTION ..... 12
1.1 REGULATORY CONTEXT ..... 12
1.2 A PRAGMATIC APPROACH TO A COMPLEX ISSUE ..... 12
1.3 SCOPE OF THE DOCUMENT ..... 13
2. HUMAN HEALTH RISK ASSESSMENT OF DISINFECTION BY-PRODUCTS (DBPS) ..... 13
2.1 INTRODUCTION ..... 13
2.2 GENERAL PRINCIPLES ..... 13
2.3 SELECTION OF MARKER DBPS ..... 16
2.4 SELECTION OF LIMITS FOR MARKER DBPS ..... 17
2.4.1 Selection of swimming and drinking water limits for marker DBPs ..... 17
2.4.2 Selection of air limits for inhalation exposure ..... 19
2.5 MARKER DBP ASSESSMENT ..... 20
2.5.1 Introduction ..... 20
2.5.2 Specific requirements for measurements of DBP levels ..... 21
2.6 RELEVANCE OF OTHER PTS ..... 23
2.7 CONCLUSIONS AND RECOMMENDATIONS ..... 24
3. ENVIRONMENTAL RISK ASSESSMENT OF DISINFECTION BY-PRODUCTS (DBPS) ..... 25
3.1 INTRODUCTION ..... 25
3.2 GENERAL INFORMATION ON DBPS ..... 25
3.2.1 Overview of reaction processes ..... 25
3.2.2 Principal groups of DBPs ..... 26
3.2.2.1 Trihalomethanes (THMs) ..... 27
3.2.2.2 Halogenated acetic acids (HAAs) ..... 27
3.2.2.3 Halogenated aldehydes ..... 27
3.2.2.4 Halogenated acetonitriles ..... 28
3.2.2.5 Halogenated amides ..... 28
3.2.2.6 Halogenated ketones ..... 28
3.2.2.7 Halogenated phenols ..... 28
3.2.2.8 Bromate ..... 28
3.2.2.9 Halogenated amines ..... 28
3.3 ENVIRONMENTAL RISK ASSESSMENT OF DBPS ..... 29
3.3.1 General principles ..... 29
3.3.1.1 Initial worst case assessment ..... 29
3.3.1.2 Group parameters ..... 29
3.3.1.3 Addressing the unknown DBPs ..... 30
3.3.1.4 Environmental risk assessment scheme ..... 30
3.3.2 Use of existing information ..... 31
3.3.2.1 Influence of pH ..... 31
3.3.2.2 Influence of substrate ..... 31
3.3.2.3 Dose, contact time and temperature ..... 32
3.3.2.4 Other relevant parameters ..... 32
3.3.3 Known DBPs to be included in the assessment ..... 33
3.3.3.1 Relevant DBP-groups and their representatives ..... 33

3.3.4 Exposure assessment ..... 34
3.3.4.1 Relevant compartments ..... 34
3.3.4.2 Exposure assessment strategies ..... 34
3.3.5 Effects assessment ..... 35
3.3.5.1 Derivation of PNECs ..... 35
3.3.5.2 Group ecotoxicity assessment ..... 36
3.3.5.3 Whole Effluent Testing (WET) ..... 36
3.3.6 Mixture toxicity ..... 37
3.3.7 Relevance of other PTs ..... 37
3.4 CONCLUSIONS AND RECOMMENDATIONS ..... 41
4. REFERENCES ..... 43
APPENDIX 1. SELECTION OF MARKER DBPS RELEVANT FOR HUMAN EXPOSURE IN SWIMMING-WATER TREATED WITH HALOGENATED DISINFECTANTS ..... 49
APPENDIX 2. SELECTION OF WATER LIMITS FOR MARKER DBPS DEEMED RELEVANT FOR HUMAN EXPOSURE IN SWIMMING-WATER TREATED WITH HALOGENATED DISINFECTANTS ..... 53
APPENDIX 3. METHODS FOR CHEMICAL ANALYSIS OF MARKER DBPS ..... 58
APPENDIX 4. POTENTIAL RELEVANCE OF PTS REGARDING THE HUMAN HEALTH RISK ASSESSMENT OF DBPS IN THE CONTEXT OF BIOCIDES AUTHORISATION (WRITTEN COMMENTING ROUND). ..... 59
APPENDIX 5. WHOLE EFFLUENT TESTING ..... 68
APPENDIX 6. SUMMARY OF INFORMATION FROM THE EU-RAR ON NAOCL ..... 70
A6.2.1 OCCURRENCE OF DBPS ..... 73
A6.2.2 RISK ASSESSMENT IN THE EU-RAR ..... 73
A6.2.3 REFINED RISK ASSESSMENT ..... 74
A6.3.1 OCCURRENCE OF DBPS ..... 75
A6.3.2 RISK ASSESSMENT ..... 77
A6.4.1 OCCURRENCE OF DBPS ..... 78
A6.4.2 RISK ASSESSMENT ..... 78

# Figures

Figure 1: Use of existing SWL and DWL for evaluating possible DBP human health risks ..... 15
Figure 2: Schematic overview of the reactions of free available chlorine with organic matter, copied from (Pickup, 2010)..... 25
Figure 3: Breakpoint curve showing the processes that occur when water is chlorinated (copied from http://water.me.vccs.edu/concepts/chlorchemistry.html) ..... 29
Figure 4: Different forms of bromine at various pH values and various concentrations of ammonia (figure copied from http://www.lenntech.com/)..... 32
Figure 5: Principle of WET..... 68

# Tables

Table 1: DBPs to be included in the human risk assessment for PT2 swimming-pool uses ..... 16
Table 2: DBP water limits to be used for 1st Tier evaluation of biocides..... 18
Table 3: DBP air limits to be used for 1st Tier evaluation of biocides..... 20
Table 4: DBPs that should be addressed in the environmental risk assessment of oxidative halogenated biocides. The relevant individual chlorinated and brominated forms are listed where applicable..... 33
Table 5: Potential relevance of PTs regarding the environmental risk assessment of DBPs in the context of biocides authorisation. ..... 37
Table 6: Trihalomethanes (THMs) ..... 53
Table 7: Bromate ..... 53
Table 8: Chlorate & chlorite ..... 54
Table 9: Haloacetic acids (HAAs) ..... 55
Table 10: Haloacetic acids (HAAs) for swimming pools ..... 56
Table 11: Halo-aldehydes (chloral hydrate and bromal hydrate) ..... 56
Table 12: Haloacetonitriles ..... 57
Table 13: Analytical methods..... 58
Table 14: Potential relevance of PTs regarding the human health risk assessment of DBPs in the context of biocides authorisation. ..... 59
Table 15: Classification scheme..... 68
Table 16: Summary of use scenarios from the EU-RAR with potential relevance for biocides authorisation. ..... 71
Table 17: Measurement of by-products of hypochlorite application in cooling water of coastal power stations, summarising data from Jenner et al. 1997..... 75
Table 18: Formation of THMs upon chlorine treatment of cooling water at different sites. Table from Berbee (1997)..... 76
Table 19: Bromoform, chloroform, EOX and AOX in cooling water from different (industrial) locations. Translated copy from Berbee (1997) ..... 77

# List of Abbreviations

| Standard term / Abbreviation | Explanation |
|---|---|
| AOX | Absorbable organic halogen |
| ANSES | French CA |
| BAT | “Biologischer Arbeitsstoff-Toleranz-Wert”: biological tolerance value for occupational exposures |
| BPC | Biocides Product Committee |
| BPR | Biocides Product Regulation |
| CA | Competent Authority |
| CAR | Competent authority assessment report |
| CEN | Comité Européen de Normalisation - European Committee for Standardization |
| COM | European Commission |
| DBA | Dibromoacetic acid |
| DBP | Disinfection by-products |
| DBP-WG | Disinfection by-products Working group |
| DCA | Dichloroacetic acid |
| DOC | Dissolved oxygen concentration |
| DOX | Dissolved organic halogen |
| DWL | drinking water limit |
| $EC_x$ | Effective Concentration at x% |
| $EC_{10}$ | Effective Concentration at 10% |
| $EC_{50}$ | Effective Concentration at 50% |
| ECHA | European Chemicals Agency |
| EOX | Extractable organic halogen |
| EPIWIN | A modelling tool |
| EU | Europe |
| EU-RAR | European Risk assessment report |
| EUSES | The European Union System for the Evaluation of Substances |
| HAA | Halogenated acetic acids |
| HAN | Halogenated acetonitriles |

| Standard term / Abbreviation | Explanation |
|---|---|
| IND | industry |
| ISO | International Organization for Standardization |
| $LC_x$ | Lethal concentration at x% |
| $LC_{50}$ | Lethal concentration at 50% |
| MBA | monobromoacetic acid |
| MCA | monochloroacetic acid |
| MS | Member States |
| NL | Netherlands |
| NOAEL | No observed adverse effect level |
| NOEC | No observed effect concentration |
| OSPAR | OSPAR Commission - Oslo Paris Convention (for the Protection *of* the Marine Environment *of* the North-East Atlantic) |
| PEC | predicted concentrations |
| PNEC | predicted no effect concentration |
| PT | Product type |
| QSAR | Quantitative Structure-Activity Relationships |
| RIVM | Dutch Competent Authority |
| RSS | Raw settled sewage |
| SE-EPA | Swedish Environmental Protection Agency |
| SPME | Solid phase micro extraction |
| SSD-approach | Species specific data approach |
| STP | Sewage treatment plant |
| SWL | swimming water limit |
| TCA | trichloroacetic acid |
| TBA | tribromoacetic acid |
| TDI | Tolerable Daily Intake |
| THM | Trihalomethane |
| TM | Technical meetings |
| TOC | Total organic carbon |
| TOX | Absorbable organic halogen |

| Standard term / Abbreviation | Explanation |
|---|---|
| TTC | Threshold of Toxicological Concern |
| TU | Toxic Units |
| $TU_a$ | Toxic Units for acute toxicity |
| $TU_c$ | Toxic Units for chronic toxicity |
| US-EPA | US Environmental Protection Agency |
| UV | Ultra-violet |
| WET | Whole effluent testing |
| WHO | World Health Organisation |
| XAD | A highly absorbent resin |

# 1. General Introduction

## 1.1 Regulatory context

The disinfection of water with oxidising biocides leads to the formation of by-products (DBPs). According to the Biocides Product Regulation (BPR), the effect of residues should be evaluated in the risk assessment (see e.g. Art. 19,(1)(b)(iii)) and according to the definition in Art. 3,(1)(h), residues include reaction products. A number of known (groups of) DBPs are biologically active, and some are (suspected) carcinogens or mutagens (e.g. chloroform, halogenated methanes, bromate). Moreover, most DBPs are more stable than the biocide itself. Therefore, a risk assessment of DBPs as part of the authorisation of biocidal products is necessary.

## 1.2 A pragmatic approach to a complex issue

The main problem for the risk assessment of DBPs is that the number of DBPs formed is very high. In drinking-water, which is the area where most of the research on the formation of DBPs has been carried out, more than 600 DBPs have currently been identified. At the same time however, more than 50% of the total organic halogen (TOX) formed during disinfection of drinking-water remains unidentified (Pressman et al. 2010; DeBorde and Von Gunten 2008). Most of this unidentified TOX is understood to be sparsely-chlorinated naturally-occurring macro-molecules that would not be expected to be bioavailable (see further in section 3.3.1.3).

For the human health risk assessment of DBPs priority was given to PT2 (swimming-water) since this is considered the most relevant from the point of view of the degree of human exposure and possible health risks. During the past decade DBP formation in swimming-pools has increasingly been studied. In one major study in indoor swimming pools in Spain in which either chlorination or bromination was used for disinfection, more than 100 different DBPs were identified (Richardson et al. 2010). The type and amount of DBPs formed in swimming-pools depends on many variables, including the availability of organic matter, the presence of (in)organic nitrogen compounds and the salinity of the water. Operating conditions, such as concentration of the active substance, the number of visitors, characteristics of the receiving water (pH, total organic carbon (TOC)) and environmental circumstances such as temperature and radiation, are all of influence (Pickup 2010; Sun et al. 2009). Due to this complexity it is very hard to predict beforehand which compounds will be formed in a specific situation and at which concentrations. Attempts were made to develop models for that purpose by Singh et al. (2012) but these have not yet led to an applicable model. In this situation only a pragmatic approach to risk assessment is feasible, in which the existing scientific knowledge on the presence of DBPs in swimming pools and of their toxicity is used in a simplified way. This approach therefore involves the selection of marker DBPs, as outlined in section 2.3. Similarly for the environmental risk assessment, a straightforward quantitative risk assessment based on PEC/PNEC comparisons for individual compounds is virtually impossible. On the other hand, a lot of research has been done in the past, which might shed light on the most commonly found DBPs and give some background on concentrations to be expected. This offers the possibility to focus on the most important (groups of) DBPs. For these DBPs, concentrations resulting from the use of active halogen-containing biocides can be compared with (existing) risk limits in order to identify potential risks.

In the future, updates of the approach will be needed as well as updates for guidance values and underlying reference values (e.g. ADI, TDI) and will be made as required, such as when new scientific data become available. If any new scientific information on DBP formation and DBP toxicity in swimming-pools becomes available, then this should be taken into account in the assessments.

## 1.3 Scope of the document

This document summarises background information and provides a strategy for the human health and environmental risk assessment of DBPs. It does not contain step-by-step instructions on how to perform the risk assessment, but defines the framework that applicants can use to build a dossier to demonstrate a safe use of the biocide under consideration. For the environmental risk assessment, the appendices include additional information that may be helpful when deciding on the risk assessment approach.

According to the mandate of the ad hoc DBP WG, the starting-point of this document is the use of halogenated oxidative biocides for three product types (PTs) that are currently under discussion for active substance approval (PT2, 11 and 12). Proposed use in PT2 comprises disinfection of swimming-pools, and disinfection of waste water. PT11 involves disinfection of cooling water, and PT12 concerns paper production. PT2 (swimming-pool) is considered the most relevant for the human health risk assessment. PT2, 11 and 12 are all considered most relevant for the environmental risk assessment because of the extent of DBP-formation in combination with direct and indirect emissions to surface water. Based on expert views, a tentative list is presented of other PTs for which the assessment of DBPs is considered relevant and some recommendations are made for future guidance development for these other PTs. The general principles of this guidance may also be useful for other groups of reactive biocides.

The strategy for the evaluation of DBPs that is proposed in this document is science-based. The implementation of the process of active substance and/or products authorisation is outside the scope of this document. Regarding procedural and/or legal issues it is recommended that applicants consult their respective Competent Authorities (CAs).

# 2. Human health risk assessment of disinfection by-products (DBPs)

## 2.1 Introduction

This section provides a general outline of the methodology to be applied to the human health risk assessment of DBPs. An important part of the approach is the identification of the relevant marker DBPs for human risk assessment for swimming-pools based on the available scientific evidence (see section 2.3). Consensus was reached on marker DBPs for specific groups of DBPs. For these marker DBPs existing limit values for water and air (for volatile compounds) were selected and agreed upon (see section 2.4). In Appendix 2 the various drinking-water limits for individual DBPs are evaluated with regard to this question. In order to perform the actual risk assessment, an assessment of the exposure is needed. Data on exposure can be retrieved via public literature (existing substances), by performing lab-scale or real life measurements (see section 2.5), using exposure models or by using anonymised existing measurements via specialised analytical labs.

## 2.2 General principles

The approach for the human toxicological risk assessment for DBPs from halogenated oxidative biocides in PT2 as described in this document, consists of simply comparing measured DBP concentration of selected DBPs to existing limits for swimming- and/or drinking-water for these DBPs. A list of existing limits is provided in section 2.4(Table 2). This list reflects the consensus reached at the workshop held on June 25 2015. As a general principle drinking-water limits are considered to be adequately protective for swimming-pools. For specific DBPs the question arises if the drinking-water limit may be over protective when used for swimming-pools. This is the case for DBPs for which dermal and inhalation exposure are low. Exposure in such cases is driven by the amount of ingested water during swimming. Because that ingested amount is lower than 2 litres

per day as assumed in the derivation of drinking-water limits, using the latter limits may be viewed as over protective. Where relevant this issue is addressed below. In principle the use of drinking-water limits should be viewed as a first tier approach which can be refined if needed with a more specific swimming-water limit. For some DBPs swimming-water limits are already available. These limits then take precedence over the drinking-water limits for that DBP. But, as agreed upon during the workshop of June 25 2015, only those swimming-water limits will be used for which the toxicological basis is known (see below). Figure 1 provides a flow diagram of the proposed method, including the possible step of further risk assessment.

As indicated above, the method makes use of existing limits for swimming- and/or drinking-water. For applying the method, consensus values must be chosen from the various existing national or international swimming-water and drinking-water limits. In addition to that, the method requires information on concentrations of DBPs in swimming-pools during use of the biocide under evaluation. The step of comparing DBP concentrations with existing limit values for swimming-water or drinking-water may be seen as the 1st tier in the risk assessment. See Figure 1 for how this first step fits into the general scheme.

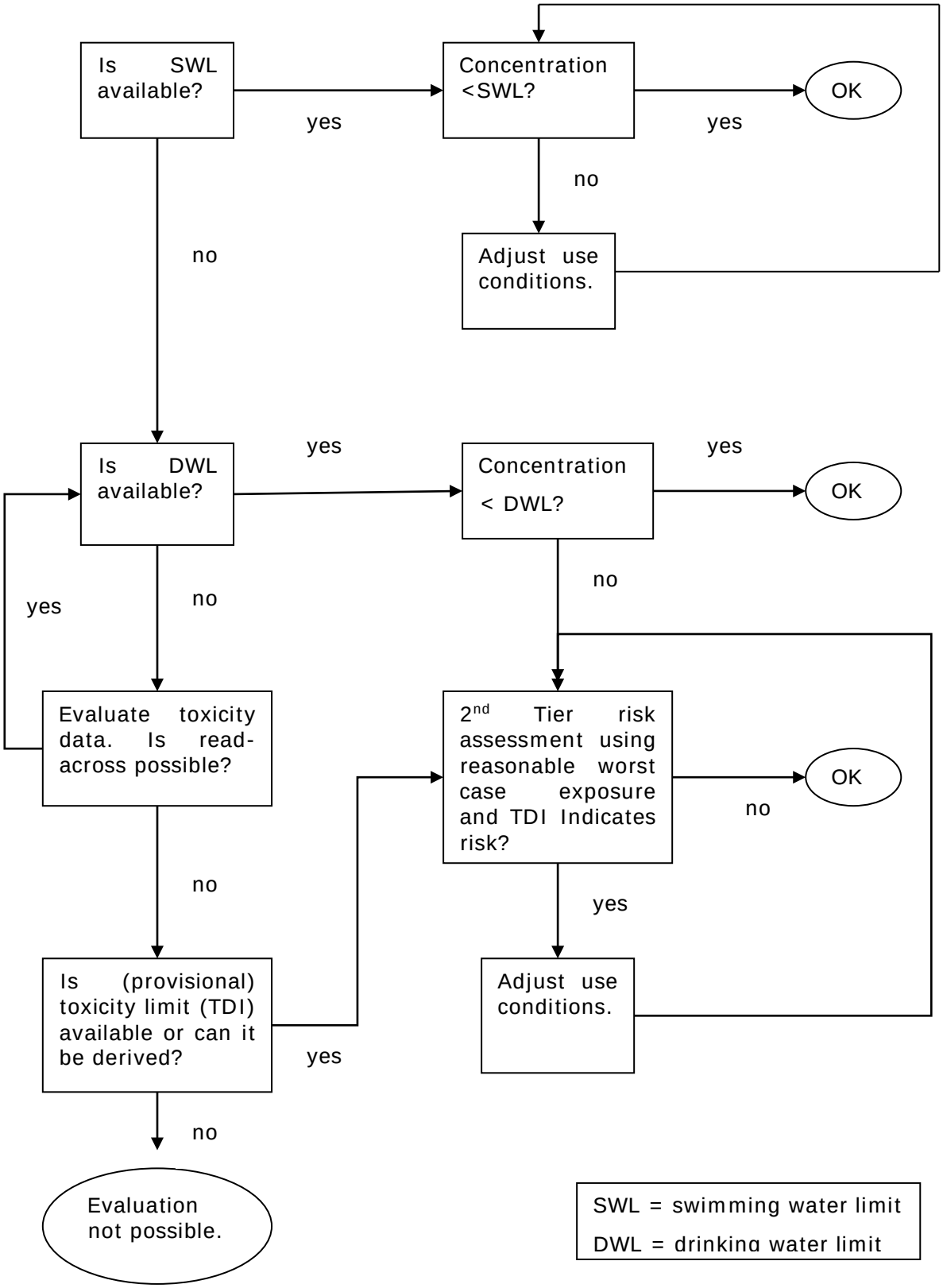
In the selection of the consensus limit value for swimming-/drinking-water, the toxicological basis for these values is an important point of consideration (critical toxic effect, NOAEL, allocation to drinking- or swimming-water). At the workshop of June 252015 it was agreed to only use limit values for which the toxicological basis is known. It was agreed that where several limit values with a known toxicological basis are available the lowest value should be chosen.

The possible 2nd tier is relevant in case existing limits are exceeded. This is especially relevant when drinking-water limits are exceeded because these limits may in some cases be over protective for exposure via swimming-water. This 2nd tier can be based on the Tolerable Daily Intake (TDI) as toxicological limit and a reasonable worst case exposure calculation for swimming-pools. One option is to derive a special swimming-water limit in this 2nd tier that can be used instead of the drinking-water limit. In appendix 2 this was for instance done for haloacetic acids because for these chemicals using a drinking-water limit most likely is over-protective. See Figure 1 for how the 2nd tier fits into the general scheme. Please note that an exposure assessment is needed for this 2nd tier, which requires additional attention.

TDIs that can be used for the 2nd tier can be selected from existing values as used by WHO in the derivation of its drinking-water guidelines (these guidelines represent by far the most extensive database as to DBPs and their toxicological evaluation). In case no value is available the feasibility of deriving an ad hoc-value based on available toxicity information should be considered. In general within the scheme, read-across is used to bridge the many data gaps known to exist at present for many DBPs. As a last resort the Threshold of Toxicological Concern (TTC) may be used to derive a tolerable intake level for use in the assessment.

It should be noted that this guidance does not address combination toxicity, i.e. additive or synergistic effects of (marker) DBPs, although it is acknowledged that this may occur. For guidance on this aspect please refer to the *Biocides Guidance Volume III Human Health, Assessment and Evaluation (Parts B+C)*, section 4.4 on Risk characterisation for combined exposures.

**Figure 1: Use of existing SWL and DWL for evaluating possible DBP human health risks**



## 2.3 Selection of marker DBPs

The evaluation of halogenated disinfectants with regard to the question which DBPs could be used as markers in the human risk assessment for DBPs in PT2, is based on the published scientific literature on this subject. The choice of these markers is inevitably pragmatic because existing knowledge concerning the chemical identity of DBPs in swimming-pools and their concentrations is incomplete. A further limitation as to the choice of usable marker DBPs is the incomplete toxicity database for many individual DBPs. Of the large number of DBPs identified at the present moment toxicity data are available for a limited number only.

Based on the information on the presence of DBPs after using halogenated oxidative disinfectants in swimming-pools as published in scientific literature, markers were selected. The result is shown in Table 1. In Appendix 1 the choice of DBPs is described in more detail.

The DBPs as presented in Table 1 reflect the current published literature on occurrence of DBPs in swimming-pools. Most likely additional unpublished data exist, as in fact was confirmed at the workshop of June 25 2015. Such additional data would be useful for further evaluation of the choice of markers. An important question is the degree to which the different groups of DBPs fluctuate relative to each other. If the different groups fluctuate in a correlated manner the number of DBPs to be evaluated could be further reduced (compared to Table 1). As of yet there is insufficient basis for such a reduction.

**Table 1: DBPs to be included in the human risk assessment for PT2 swimming-pool uses**

| Compounds | Notes |
|---|---|
| Trihalomethanes (THMs) | THMs are quantitatively the most important group of DBPs. Formation of either the chlorinated or brominated THMs will dominate depending on the source levels of active chlorine or active bromine present in the treated water. |
| Bromate | Formed after ozonation of water containing bromide. When bromide-containing water is disinfected by chlorination, formation of bromate also occurs. Use of brominated disinfectants is also expected to lead to increased bromate levels. |
| Chlorite and chlorate | Frequently found in swimming–water. Concentrations often in the mg/L range. |
| Haloacetic acids (HAAs) | HAAs are quantitatively 2$^{nd}$ most important group of DBPs. When bromide concentrations are low, mono-, di- and trichloroacetic acid are dominant, but brominated analogues (mono-, and dibromoacetic, bromochloroacetic acid) are present when bromide concentrations are higher. After use of brominated active ingredients brominated acetic acids are also expected to be present. |
| Haloaldehydes | Based on reviewed literature trihaloacetaldehydes (chloral hydrate and bromal hydrate) are relevant. |
| Haloacetonitriles | Dihaloacetonitriles are most important within this group based on reviewed literature. Dibromoacetonitrile formed in the |

| | |
|---|---|
| | presence of bromide. |
| Haloamines | Based on reviewed literature trichloramine is the most important DBP, especially for the air compartment in indoor swimming-pools. |

## 2.4 Selection of limits for marker DBPs

Exposure to DBPs in swimming-pools occurs via the oral route (accidental water ingestion), via the skin and via inhalation. In deriving swimming-water limits for DBPs all of these exposure routes should be taken into account, i.e. the total calculated systemic exposure for a swimmer needs to be used. For the swimming-water limits as presented in Table 2 such a calculation of the total systemic exposure was done. A possible additional health effect, however, which is not covered by this calculation, is the potential route-specific local toxicity (irritation etc.) of the airways by DBPs. For these specific DBPs inhalation limits need to be selected.

### 2.4.1 Selection of swimming and drinking water limits for marker DBPs

As stated earlier in this document, the method requires a consensus list of existing swimming- and/or drinking-water limits for the selected marker DBPs. Table 2 below provides a list of values. This table reflects the consensus as reached at the workshop of June 25, 2015. Only limits for which the toxicological basis was known were selected. Where more than one limit was available for which the toxicological basis was known the lowest value was chosen. During the workshop it was decided that limits (both SWL and DWLs) need to be reviewed every 5 years and earlier if needed.

In Appendix 2 the choice of water limits for the different marker DBPs is explained in more detail.

Concerning the drinking-water limits, during the workshop of June 25, 2015, the question was raised whether these limits would not be under protective in cases where exposure via swimming-water is high due to dermal and inhalation exposure. Conversely drinking-water limits may be overprotective in case the oral route is the only route in the swimming-pool situation (for non-volatile DBPs with low potency for dermal penetration). These points are discussed for individual marker DBPs in Appendix 2. For haloacetic acids this led to new swimming-water limits. These were derived because for these DBPs drinking-water limits are considered over-protective. See Appendix 2 for discussion. For chloral hydrate and bromal hydrate and for the relevant haloacetonitriles drinking-water limits were found to be adequately protective.[3]

[3] As explained in Appendix 2, inhalation exposure to these DBPs (chloral hydrate, bromal hydrate, haloacetonitriles) in swimming-pools is expected to be relatively low based on their Henry coefficients so using drinking-water limits for these DBPs may be considerd a worst case approach. In case of exceedance of the drinking-water limits 2nd tier evaluation may be appropriate, including exploration of the possibility of deriving a swimmimg-water limit for these DBPs based on exposure calculations.

**Table 2: DBP water limits to be used for 1st Tier evaluation of biocides**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Trichloromethane (chloroform) | ΣTHMs: 50[4] (chloroform equivalents)[5] | Swimming-water limit The Netherlands | TDI for chloroform, cancer risk estimation for BDCM, based on exposure calculation oral+dermal+inhalation |
| Tribromomethane (bromoform) | | | |
| Bromodichloromethane | | | |
| Dibromochloromethane | | | |
| Bromate | 100 | Swimming-water limit The Netherlands | Bromate is genotoxic carcinogen, value chosen based on extra cancer risk of $10^{-5}$ per lifetime as reference based oral exposure during swimming (dermal and inhalation considered negligible) |
| Chlorate & chlorite | Σchlorate/ chlorite: 30000 | Swimming-water limit Germany Swimming-water limit The Netherlands | Based on TDI based on oxidative damage of blood cells as critical effect |
| Monochloroacetic acid | 800 | Swimming-water limit derived in the present document | Based on TDI as reported by WHO, 20% of TDI allocated to swimming-water |
| Dichloroacetic acid | 1500 | Swimming-water limit derived in the present document | Compound is genotoxic carcinogen, extra lifetime cancer risk level of $10^{-5}$ as reference |
| Trichloroacetic acid | 8000 | Swimming-water limit derived in the present document | Based on TDI as reported by WHO, 20% of TDI allocated to swimming-water |
| Monobromoacetic acid | 800 | Read across from | Read across from |

[4] The derivation of the Dutch swimming-pool limit of 50 ug/litre [for THM] was based on exposure calculations. Chronic exposure for swimmers was estimated for a proposed THM-level of 50 ug/litre in swimming-pool water. The guidance value (in Table 2) is for swimmimg-pools and is not seen to be in conflict with the official EU drinking-water limit, although the potential problem of exceeding TLV values is recognized. Such problems should be addressed at a National level until relevant CA evaluations and discussions of product authorisations can be considered.

[5] Chloroform equivalents calculated by multiplying the concentration of the THM in question with the ratio of the molecular mass of chloroform divided by the molecular mass of the THM in question. For example, if 10 µg/L of DBCM is detected, the equivalent concentration as chloroform would be (mwt chloroform/mwt DBCM) x 10 µg/L = 5.7 µg/L.

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| | | monochloroacetic acid | monochloroacetic acid |
| Dibromoacetic acid | 1000 | Read across from dichloroacetic acid | Read across from dichloroacetic acid |
| Tribromoacetic acid | 8000 | Read across from trichloroacetic acid | Read across from trichloroacetic acid |
| Dibromochloroacetic acid | 8000 | Read across from trichloroacetic acid | Read across from trichloroacetic acid |
| Chloral hydrate | 100 | WHO drinking-water guideline | TDI based on liver effects, 80% of TDI allocated to drinking-water, drinking-water consumption 2 L per day |
| Bromal hydrate | 100 | Read across from chloral hydrate | Read across from chloral hydrate |
| Dichloroacetonitrile | 20 | WHO drinking-water guideline | TDI based on liver effects, 20% of TDI allocated to drinking-water, drinking-water consumption 2 L per day |
| Dibromoacetonitrile | 70 | WHO drinking-water guideline | TDI based on growth effects, 20% of TDI allocated to drinking-water |
| Bromochloroacetonitrile | 20 | Read across from dichloroacetonitrile | Read across from dichloroacetonitrile |

To add to the usefulness of the guidance, for the selected marker DBPs the suitable methods for chemical analysis in swimming-pool water are given in appendix 3.

### 2.4.2 Selection of air limits for inhalation exposure

Based on the literature on the subject, THMs and trichloramine are considered as volatile DBPs for which this issue is potentially relevant.

For THMs however, the potential for inducing local irritation in the airways is relatively low (US-EPA 2012, EU 2008) and at the concentrations as measured in swimming-pools of a maximum of around 200 µg/m$^3$ (RIVM 2014), such effects are not likely. Thus, for THMs using the swimming-pool limit of 50 µg/L in the assessment may be considered to be protective also with regard to possible inhalation effects after release of the THMs to swimming-pool air.

Trichloramine is strongly irritating for airways and available literature clearly indicates this DBP to be associated with adverse respiratory effects in swimmers and pool attendants in indoor swimming-pools (see Appendix 1). By comparing measured air concentrations with an appropriate existing limit value in air the potential risk for local inhalation effects can be evaluated. In France a maximum of 500 µg/m$^3$ has been in use from 1995 onwards (Hery et al. 1995) but ANSES and INRS now use a lower value of 300

µg/m$^3$ (ANSES 2012). RIVM (2014) proposed using the 500 µg/m$^3$ as maximum with a target value of 200 µg/m$^3$. These values are all based on epidemiological surveys[6] in which concentrations of trichloramine measured in swimming-pool air were correlated with respiratory health complaints among pool workers. Such surveys provide a rough indication only as to the exact concentration-effect relationship and consequently the air limits mentioned have relatively low reliability.

No data are available for tribromamine but by extension this DBP may also be considered relevant for air.

**Table 3: DBP air limits to be used for 1st Tier evaluation of biocides**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Trichloramine (air) | Maximum 300 µg/m$^3$; Target value 200 µg/m$^3$ | ANSES (France), proposed Dutch air target value for indoor pools | Epidemiological surveys among pool workers |
| Tribromamine (air) | Maximum 300 µg/m$^3$; target value 200 µg/m$^3$ | Read across from trichloramine | Read across from trichloramine |

In principle exposure to non-volatile DBPs is possible via aerosol formation. It is noted that this route (aerosolization) probably is relatively unimportant in the overall exposure to DBPs in PT2. This issue can be addressed based on two studies in which aerosol formation during showering was examined. Xu and Weisel (2003) studied exposure through aerosol formation during showering with water contaminated with haloacetic acids and haloketones. For HAA water concentrations of 249-300 µg/L they calculated a daily exposure via aerosol during 10 minutes' shower of less than 1 µg/day. Zhou et al. (2007) also studied aerosol formation during showering. They measured a total aerosol particle concentration inside a shower of 5-14 mg/m$^3$. Using the latter range it can be calculated that a high concentration of 1000 µg/L DBP in water would lead to a total exposure concentration via aerosol of only 14 ng/m$^3$. Note that of the total aerosol only part would be inhalable. This supports the idea that aerosol formation is a minor exposure route only for PT2.

## 2.5 Marker DBP assessment

### 2.5.1 Introduction

To perform a risk assessment as described above, an assessment of marker levels is needed. Aspects relevant for a representative assessment of the selected marker DBP's are identified below.

It is general knowledge that conditions influencing the formation of DBPs vary considerably in different swimming-pools. It is not possible to cover all these variables in the assessment. It is not feasible to require measurements for all conditions reflecting all

[6] References: Hery et al. (1995), Jacobs et al. (2007), Parrat et al. (2012), Nordberg et al. (2012), Fantuzzi et al. (2013)

potential variations of parameters. Further, it is acknowledged that not only the technical design of the swimming pool influences these parameters, but also the facility management applied by the swimming pool holder.

Relevant information on marker DBPs can be provided in three ways:

1. Much published and unpublished information on the formation of DBPs in swimming pools is available which can be used as a basis for the exposure assessment. This information should be collected and reviewed by the applicant**;**
2. An initial assessment can be based on simulation and modelling;
3. Actual measurements should be performed if no data are available or available data are of insufficient quality. A combination of these three approaches is preferable. It is primarily up to the applicant and the reviewing competent authority to assess what is needed in individual cases.

At the workshop, consensus was reached for active substance approval that, in the absence of sufficient data from literature, measurements performed under defined conditions and in at least one “representative” pool, are required. The basic requirement for the DBP guidance is that the applicant must generate information relevant for human health and which is sufficient for the evaluation of the possibility of DBP formation in the vast majority of swimming pools within the EU, inclusive of pool size and type. Currently, a dossier that has full reliance on the acceptance of a biocidal product based on a model pool to provide relevant information related to practice on a set of key DBP’s, is not feasible. Note that extra care should be given to product authorisations for seawater swimming-pools because a different spread in marker DBPs will be present in these pools compared to fresh water swimming-pools.

Several oxidative halogenated disinfectants are already on the market. Therefore, measuring under actual use conditions should be possible. Applicants can approach specialised analytical labs for consultation. These labs have all the required information on measurements of DBPs under specified uses and conditions and are able to process the (anonymised) existing data for existing substances. These consultants are experts in translating the measurements to defined use conditions in representative swimming pools.

For new substances, not yet on the market, measuring under actual use conditions seems more difficult. For these substances, initial measurements can be performed by modelling and/or read across. The data that are generated by modelling will be subject to expert judgement by national authorities. Where needed a temporary authorisation for testing in practice (i.e. conducting measurements in at least one “representative” fully operational pool) can be opted for at the national authorisation level.

### 2.5.2 Specific requirements for measurements of DBP levels

- The information necessary for the assessment should be generated in tests in actual pools in which the swimming-water is shared by a number of swimmers;
- The pool must be operated with defined, standard equipment and have flow conditions that are generally applied and which are essential for maintaining pool water quality. It should exclude non-standard equipment which impacts on pool water quality, be it negative or positive;
- Measurements should take into account operational conditions which substantially increase the risk for DBP formation and which may exist in swimming pools, either temporarily or permanently, yet fall within operational limits that are considered acceptable practice, legally or otherwise;

- Measurements should exclude operational conditions which minimise the risk for formation of DBP's, but would fall within operational limits that are considered acceptable, legally or otherwise;
- The evaluation period should be long enough and parameters must be measured sufficiently frequently to adequately reflect variability;
- Type of pool: selected marker DBP's should be measured in a competition pool[7], a recreational pool, and a toddler pool because experience shows levels are different in these types of pools. The question whether a separate assessment is necessary for salt water pools should be addressed on a case-by-case basis based on available information (relevance depends on the halogenated disinfectant used);
- Pool equipment and flow conditions: The relevant basic standard equipment in swimming-pools is sand filters or sand/activated coal combi filters. These are standardly complemented with a flocculation system and – more or less standardly - separate activated coal filters. In many countries, operational conditions for filtration equipment are also specified or recommended (filter backflush velocity, duration, and frequency). Equipment for the in-situ formation of disinfectants mostly is considered standard. Pools must be equipped with controlled dosing systems for all chemicals to ensure operational stability, have a flow rate which meets the legally required maximum residence times in pools, and meets the limits for pH and recommended disinfectant concentrations of swimming water throughout the pool. Additional equipment such as ozone and UV systems are not standard equipment and might positively or negatively affect the degree of marker DBP formation. To ensure the general relevance of the assessment it should be carried out only in pools equipped with this standard equipment;
- Operational conditions:
    - The directly controllable legal parameter limits for swimming-pools specified in most EU countries and which have an impact on the concentration of marker DBP's in swimming-water include pH (7.3 ± 0.3-0.5, depending on member state), disinfectant concentration, and average fresh water supply per swimmer. They must be monitored because together with requirements for pool equipment as described above, they constitute good pool practices;
    - Chemical parameters for which the limits are also specified but which are not directly controllable are permanganate levels and in some countries urea levels also. The values of these parameters also have an impact on the concentration of marker DBP's in swimming water: they represent the organic the inorganic load respectively brought by swimmers into the swimming-water and therefore must be monitored;
    - The realistic worst case-scenario for marker DBP formation will be realised when a minimum suppletion of fresh water per swimmer is combined with a maximum number of swimmers per day in the pool for a prolonged period. If the opposite conditions were used during monitoring (i.e. a very low level of pool use) the assessment would be of no value, as no legal limits exist for the minimum number of visitors in a pool per day, nor for the maximum fresh water supply per swimmer. Most EU countries specify a minimum suppletion water of 30L per swimmer. The maximum number of swimmers allowed is less

[7] Indicational sizes (variation is possible): Competitional (length) 25-50 m x (width)18-25 meter x (depth) 1.8-2.5 meter; Recreational pool: depth >0.5 m, other measures vary greatly; toddler pool: depth <0.5 m, other measures vary greatly.

uniform, but a value of around 50 swimmers per day per 100 $m^3$ swimming water is quite common. These considerations should be important criteria for the selection of pools suitable for a representative marker DBP risk assessment.

- In general the frequency at which the recommended "good pool practice" parameters and the selected marker parameters should be analysed, depends on how fast their values changes. For example, parameters like disinfectant concentration and pH are commonly measured a few times per day, whereas parameters like chlorate and bromate change very slowly with good pool practice and commonly are measured on a monthly basis only. Recommended frequencies for bromate, THMs and trichloramine are 2-4 times per year (limited fluctuation). Appropriate frequencies for other selected marker DBP's like HAA's will depend on what is found in practice, depending on the degree of fluctation. Some MSs have recommended frequencies for all specified parameters (e.g. Dutch Ministry of Infrastructure and the Environment (Pool Water Treatment 2015, under consultation);
- Samples for the analyses must be taken in the most unfavourable place in the pool. This place can be determined using a colour test according to CEN 15288/2. These, for example, are places which are the least refreshed by the circulating water and/or near or between two outlets (approximately 30 cm under the surface);
- The duration measurements must be four consecutive months at least. No test period should start within four months after major changes in the pool operation have taken place (i.e. new filter beds);
- Useful additional data for the applicant: To ensure that good pool practices have been followed throughout the test period, the applicant should ue the analyses for the chemical parameters (that are part of good pool practices), together with the easily measurable chloride and nitrate concentrations in swimming water. These constitute a useful finger print for the applicant to monitor the extent of good pool practices during the test period, and give insight into which operational parameters should be improved upon during the test period.

## 2.6 Relevance of other PTs

The present guidance has been developed to be applicable to biocides in PT2, but the human health risk assessment of DBPs may be relevant for other PTs as well. To focus future work, the workshop participants were asked to indicate for which PTs a human health risk assessment of DBPs would be necessary. The results of the written consultation round are presented in Appendix 4. From this inventory, it appears that PTs 1, 3, 4 and 5 are considered most relevant from the perspective of human health risks of DBPs. Please note that this is a tentative list since only few responses were received. Also note that relevance in this context is related to potential DBP-formation as a direct result of the use of halogenated oxidising biocidal active substances in a particular PT. It is recognised that many processes operate on potable water. Potable water may contain DBPs due to prior disinfection, but these are not considered to be associated with the biocide itself. All water for human consumption is treated in line with the Drinking Water Directive and Regulations. Comparative standards are applied across EU.

During the breakout session for human health at the workshop in June 2015 priority levels were given to the different PTs as a further attempt of ranking the PTs for future guidance development. Highest priority was given to PT2, 4 and 5 with little priority being given to PT11 and 12 and a very diverse distribution of priority was demonstrated for PT3. PT1 was given the label "no priority", however during the break out session it was pointed out that PT1 does have a direct exposure pattern for active chlorine use.

This guidance could be used as a starting-point for other PTs. However, other PTs will have different starting materials, pH, temperature etc. and this will affect which DBPs are formed. Depending on the PT, the selection of the marker DBPs could be very different from those now selected for swimming-water. Therefore, for the other PTs future development of an adapted guidance is needed to ensure a harmonised approach across the EU.

## 2.7 Conclusions and recommendations

This document provides a scientific and pragmatic strategy for the risk assessment of disinfection by-products (DBPs) in the context of biocides authorisation under European legislation.

The risk assessment is based on a set of known marker DBPs, using consensus health-based limit values and published, modelled or measured DBP concentrations under described conditions.

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, haloaldehydes (chloral/bromal hydrate), trihalogenated amines chorites and chlorates. In principle all selected marker compounds listed in these DBP-groups should be addressed in the risk assessment. Specific compounds may be excludedif justified; additional DBPs should be included if there are indications from e.g. measurements or theoretical considerations that a particular active substance leads to their formation.

Measurements of concentrations of DBPs after biocide use in swimming-pools are needed to perform the risk assessment. Relevant concentration data may be gathered from available literature. Where needed actual measurements should be performed. Simulation studies or modelling can be used to derive realistic worst case formation levels. Simulation or modelling approaches should be part of a robust argumentation and a full rationale should be given in the case of extrapolating data from one situation to another. Most marker DBPs that should be addressed in the risk assessment are relevant for several active substances and/or applicants. It is recommended that industry parties coordinate activities to refine the risk assessment of the known marker DBPs. Existing information should be used where possible and the applicability to the present situation should be demonstrated.

The present guidance focuses on PT2 for which human exposure was considered most relevant in view of the extent of exposure to DBPs. Other PTs for which a DBP-assessment may be needed are PT1, PT4 and PT5, followed by PT3, PT11 and PT12. It is recommended to further investigate the applicability of the present guidance to these PTs.

# 3. Environmental risk assessment of disinfection by-products (DBPs)

## 3.1 Introduction

This section provides a general outline of the methodology to be applied to the environmental risk assessment of DBPs. Section 3.2 gives some general information on DBP formation from an environmental perspective. The environmental risk assessment is discussed in section 3.3. Section 3.4 gives a tentative list of other PTs for which a DBP-assessment is considered relevant. Conclusions and recommendations are listed in section 3.5.

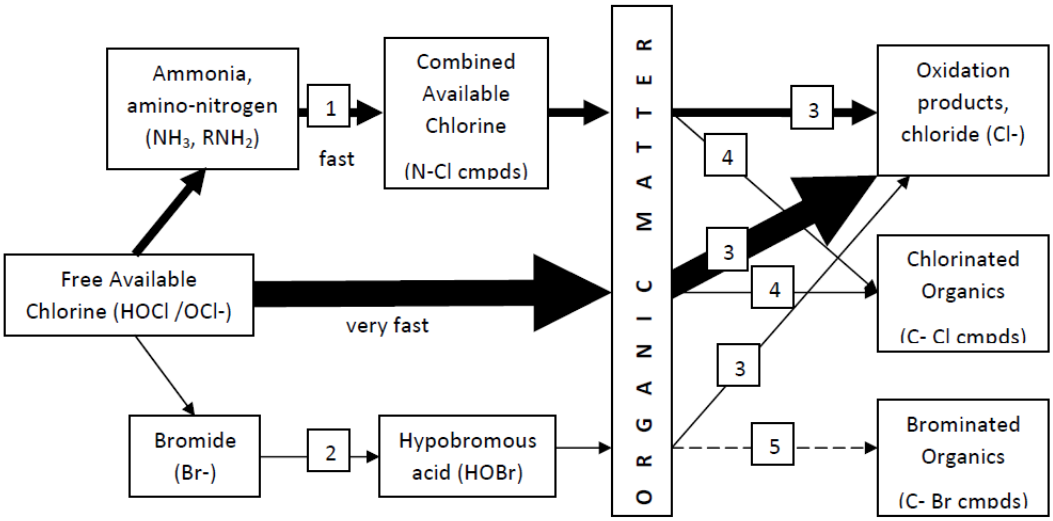
## 3.2 General information on DBPs

### 3.2.1 Overview of reaction processes

Most of the information on DBPs refers to situations in which chlorination is used for disinfection treatment, but in general the principles are applicable to bromination as well. The extent to which different compounds are formed may differ, depending on the competition of bromine with chlorine in substitution reactions. For illustrative purposes, a summary of the reactions of free chlorine is presented below in Figure 2, copied from a publication by Euro Chlor (Pickup, 2010).

**Figure 2: Schematic overview of the reactions of free available chlorine with organic matter, copied from (Pickup, 2010)**

Key:
cmpds = compounds.
Numbers represent different pathways mentioned in the text below.
Bold arrows represent the major pathways.




The following accompanying text is copied from this report:

> 'The dominant reaction of active chlorine is oxidation of organics (and also reducible inorganics), generally rapid reactions (3) which result in the chlorine being mineralised as chloride. Active chlorine also reacts rapidly with amino-nitrogen atoms (1) that are frequently present in proteins or amino acids in natural organic matter, and with ammonia. The products will be N-chloramines, mainly labile, inorganic species that are often collectively referred to as 'combined available chlorine', for they can subsequently undergo parallel reactions to the original 'free' active chlorine

predominantly yielding oxidation products (3). The focus of this dossier, however, is on the subsidiary reaction pathway by which active chlorine, and to a lesser extent the intermediate combined chlorine, can chlorinate organic molecules forming carbon-chlorine (or carbon-halogen) bonds to produce halogenated organics (4). In the presence of bromide ion, some active chlorine reacts initially to produce hypobromous acid (2) which then produces oxidation products releasing the bromide (3) again with the formation of small quantities of brominated organics (5) as a side reaction.'

In case bromine is used as active substance pathways 3 and 5 will become more important. The formation of brominated organic compounds will also become highly relevant when bromide is present in the treated water (e.g. saltwater), and not be restricted to 'small quantities' as suggested above.

It is also noted by (Pickup, 2010) that

'in the presence of significant quantities of amino-nitrogen, which is present in organic matter encountered in most uses, almost all the chlorine is more or less rapidly mineralised to chloride: only a few per cent at most is incorporated into carbon-halogen bonds. In clean systems, however, such as drinking water and swimming pool disinfection where low levels of free chlorine are constantly maintained, up to perhaps 25% of the limited amounts of chlorine involved can become bonded to carbon. In acid pH bleaching of paper pulp, of the order of 10% of the applied chlorine was typically converted to halogenated organics [Solomon 1993].'

### 3.2.2 Principal groups of DBPs

This section gives an overview of the most prominent (groups) of DBPs resulting from the use of oxidative disinfectants and provides some background information on the groups (mainly based on Berbee, 1997; EC, 2007; Pickup, 2010; Richardson et al., 2010; ). Only brominated or chlorinated compounds are discussed here. There is almost no information on the formation of iodinated DBPs. Iodoform was detected in a small drinking water disinfection plant applying chlorine dioxide (Richardson et al., 2003) , but no iodinated DBPs were detected in bromine or chlorine-treated swimming pools in Spain (Richardson et al., 2010). The use scenario assessments in the EU-RAR (EC, 2007) show that for hypochlorite most applications studied generate a similar spectrum of by-products in amounts that have a similar quantitative distribution. Some observations are summarised here and commented on where necessary, specific DBP-groups are further discussed in more detail below.

- The dominant DBP families are the trihalomethanes (THMs) and the haloacetic acids (HAAs)
- Several 'second tier' families are present typically at an order of magnitude lower concentration e.g. haloaldehydes, haloketones and haloacetonitriles
- Overall, in any specific scenario, there are likely to be several hundred different small organohalogen molecules formed at concentrations orders of magnitude lower again such that their total is still at most a few per cent of the total. It is often stated that a substantial proportion, perhaps half of the organohalogen formed, remains unidentified. The assessment of the unknown fraction is further addressed in section 3.3.1.3.
- In applications where there are substantial quantities of amino-nitrogen (e.g. protein substrates), organic N-chloramines will be formed. These are not long lived, and are part of the measurable 'combined available chlorine' but will normally also be detected as 'organohalogen' in group parameters such as AOX (absorbable organic halogens) or TOX (total organic halogens). The halogen, however, is contained in N-halogen bonds rather than C-halogen bonds which

were the historical focus of concern. Still, it is considered necessary to include them in the assessment if they are formed (see 3.3.3.1).

- Historically there was concern about the formation of high-hazard molecules, in small but ecotoxicologically significant quantities, such as polyhalogenated dioxins and furans. This was particularly associated with the bleaching of paper pulp which took place at acid pH. The EU-RAR notes that such molecules are not formed in detectable quantities at neutral or alkaline pH, which are the pHs at which current uses of hypochlorite are focused
- Formation of other polychlorinated species, especially aromatics, which were potentially persistent and bioaccumulative, was also a concern in the pulp-bleaching application, partly because of the aromatic substrates present. Traces of phenols were found in the past. Again, given the substrates typically present in current applications, formation of such molecules is found to be insignificant at neutral or alkaline pH.

#### 3.2.2.1 Trihalomethanes (THMs)

The four representatives of this group are chloroform (trichloromethane), bromoform (tribromomethane), dichlorobromomethane and dibromochloromethane. Each of these four compounds can be formed. When bromide concentrations are low, chloroform is the dominant compound, while in seawater bromoform is dominant (Berbee, 1997; Pickup, 2010) . All four THMs are volatile, volatility decreases in the order $CHCl_3$ > $CHBrCl_2$ > $CHBr_2Cl$ > $CHBr_3$. Solubility decreases in the same order from 8 g/L for chloroform to 3 g/L for bromoform (EpiWin). Log Kow-values range across this series from 1.97 for $CHCl_3$ to 2.4 for $CHBr_3$. They are removed in sewage treatment plants by volatilisation (Pickup, 2010) . Trihalomethanes are regulated under EU drinking water legislation (EC, 1998) , the drinking water standard for total THMs is 100 µg/L, but MSs may have set limits on a national level.

#### 3.2.2.2 Halogenated acetic acids (HAAs)

This group consists of nine different chlorinated/brominated acetic acids. The five most common are monochloroacetic acid (MCA), dichloroacetic acid (DCA), trichloroacetic acid (TCA), monobromoacetic acid (MBA) and dibromoacetic acid (DBA). Together, these five are referred to as $HAA_5$. The sum of bromodichloroacetic acid (BrCl2AA), dibromochloroacetic acid (Br2ClAA), and tribromoacetic acid (Br3AA) concentrations is known as $HAA_3$. $HAA_6$ refers to the sum of $HAA_5$ and bromochloroacetic acid (BrClAA) concentrations. $HAA_6$ and $HAA_3$ together make up $HAA_9$. When bromide concentrations are low, MCA, DCA and TCA are dominant, but brominated analogues (MBA, DBA, bromochloroacetic acid) may be present when bromide concentrations are higher [Ref.:6]. Haloacetic acids are relatively polar, non-volatile, water soluble species. Solubility in water at normal temperatures is of the order of 1000 g/L for TCA increasing to 6000 g/L for MCA, DCA is a miscible liquid. Octanol/water partition coefficients range from 1.33 for TCA down to 0.22 for MCA (data from HSDB, cited in (Pickup, 2010) ). The haloacetic acids are to varying degrees biodegradable, the most recalcitrant being TCA.

#### 3.2.2.3 Halogenated aldehydes

The most commonly known representative of this group is chloral hydrate (trichloroacetaldehyde), other chloro- and bromo-substituted acetaldehydes (dichloro, bromochloro etc.) are also reported (Richardson et al., 2003; 2010) . Laboratory data show halogenated aldehydes can be produced by chlorinating humic and fulvic acids (citation in Pickup, 2010). Trihaloacetaldehydes hydrolyse to the corresponding THMs. Reported half-lives for haloacetaldehydes in water are 2 to 6 days at neutral pH and ambient temperatures, stability decreases as pH and temperature increases (Pickup, 2010) .

#### 3.2.2.4 Halogenated acetonitriles

The four haloacetonitriles most commonly reported as by-products of active chlorine use are dichloroacetonitrile, trichloroacetonitrile, chlorobromoacetonitrile and dibromoacetonitrile (Pickup, 2010) . As for the above mentioned groups, brominated compounds are formed in the presence of bromide. Preliminary evidence exists that increased levels of halogenated acetonitriles are associated with the use of chloramine for disinfection instead of chlorine (Plewa et al., 2008). Haloacetonitriles are relatively volatile, the mono-derivatives being most volatile and bromo-derivatives less volatile. In chlorinated drinking water, haloacetonitriles levels are typically an order of magnitude lower than THM levels, and below 5% of total halogenated by-products (Pickup, 2010). The haloacetonitriles are relatively susceptible to hydrolysis, via haloacetamides to form haloacetic acids, the rate of hydrolysis rising with increasing pH and number of halogen atoms in the molecule (citation in Pickup, 2010).

#### 3.2.2.5 Halogenated amides

This group, which consists of chlor- and bromacetamides, have been detected in drinking water and swimming pools (Pickup, 2010; Plewa et al., 2008; Richardson et al., 2010). As for halogenated acetonitriles, the use of chloramines is indicated as a potential cause of formation, either direct or via hydrolysis of the acetonitriles (Plewa et al., 2008).

#### 3.2.2.6 Halogenated ketones

These compounds, of which 1,1-dichloropropanone, 1,1,1-trichloropropanone, and bromopropanone are representatives, may be formed by reactions with humic and fulvic acids (Pickup, 2010) . They have been detected in drinking water and swimming pools (Pickup, 2010; Richardson et al., 2010). According to studies cited in Pickup, 2010, haloketones are relatively volatile and are susceptible to hydrolysis.

#### 3.2.2.7 Halogenated phenols

As for the ketones, chloro- and bromophenols may be formed by reactions with humic or fulvic acid (Pickup, 2010). After initial addition leading to monochloro- or bromophenol, further addition leads to di- or tri- halogenated phenols. In the Euro Chlor report (Pickup, 2010), it is suggested that formation of the tetra- or penta-forms is probably not likely, they have not been identified in swimming water (Richardson et al., 2010). Chlorinated phenols are moderately to highly lipophilic, volatility is relatively low.

#### 3.2.2.8 Bromate

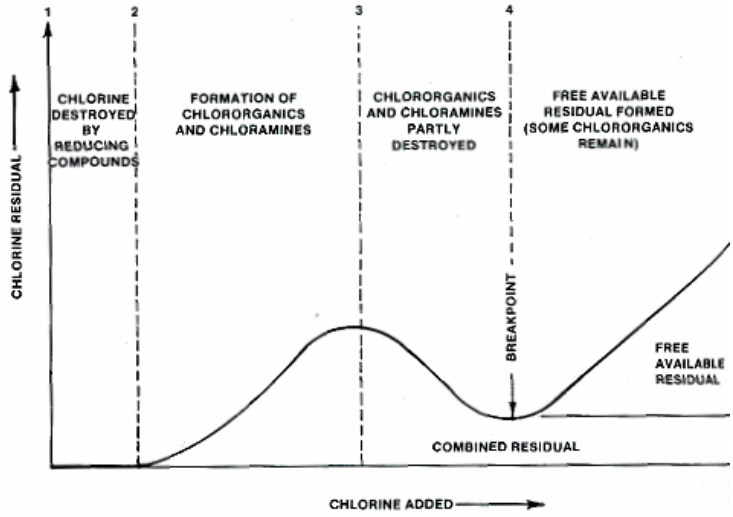
Bromate can be formed when high levels of free available chlorine are present in combination with a high pH, and when bromide is present (Berbee, 1997). It should also be noted that bromate may be present in sodium hypochlorite, the EU-RAR (EC, 2007) mentions a range of 3-45 mg/kg as sodium bromate (ca. 2.5-38 mg/kg as bromate), with levels up to 90 mg/kg (ca. 77 mg/kg as bromate), a range of 34-37 mg bromate/kg is mentioned in (Berbee, 1997) . Bromate is regulated under EU drinking water legislation (EC, 1998) , the drinking water standard is 10 µg/L.

#### 3.2.2.9 Halogenated amines

This group consists of chloramines and bromamines. These compounds are formed when amines ($R\text{-}NH_2$) or ammonium $NH_4^+$ is present. Most of the halogenated amines initially formed, notably monochloramine, are labile, and can react subsequently given long contact times to produce DBPs (Pickup, 2010) . In case there is a large excess of active chlorine over $R\text{-}NH_2$, chloramines like $R\text{-}NCl_2$ and $NCl_3$ are formed; $NCl_3$ is a very volatile product (EC, 2007). The formation of chlor- and bromamines can be seen as an intermediate stage in the chlorination process. Monochloramines are mainly formed in bromide-poor freshwater, whereas brominated amines are formed in brackish and saltwater. When further dosing of chlorine or bromine results in excess of free chlorine

(so-called breakpoint chlorination), amines are partly degraded (Berbee, 1997). Chlorinated amines are included in the determination of Total Residual Oxidant (TRO; synonyms: total residual chlorine, total chlorine, total available chlorine), which is often used to express dosages or oxidative strength of an effluent. In contrast, they are not included in the free chlorine fraction (also called free available chlorine). Nitrosamines may be formed upon drinking water treatment by chloramination (Mhlongo et al., 2009).

**Figure 3: Breakpoint curve showing the processes that occur when water is chlorinated** (copied from http://water.me.vccs.edu/concepts/chlorchemistry.html)




## 3.3 Environmental risk assessment of DBPs

### 3.3.1 General principles

#### 3.3.1.1 Initial worst case assessment

The environmental risk assessment of DBPs basically follows the principles of the environmental risk assessment for biocidal active substances in which predicted concentrations (PECs) are compared with a predicted no effect concentration (PNEC) for the ecosystem. This so-called PEC/PNEC approach is only feasible for identified ('known') DBPs for which the environmental exposure and (no) effect levels can be quantified. Section 3.3.3 gives more information on the known DBPs that should be addressed in the risk assessment. To prevent unnecessary evaluations for these known DBPs, a simple worst-case strategy may be followed in the first instance precluding further assessment if the outcome is that no risk is expected. For this, the PEC for the most toxic known DBP (i.e. the known DBP with the lowest PNEC) is recalculated from the PEC for the biocidal active substance by assuming 100% conversion (taking account of stoichiometry and molar weight aspects). If this leads to a PEC/PNEC <1, further assessment (also for less toxic DBPs) is not necessary; see section 3.3.5.1 where the derivation of PNECs is explained.

#### 3.3.1.2 Group parameters

The formation of DBPs is often characterised by measuring (the increase) in group parameters such as TOX (total organic halogens) or AOX (adsorbable organic halogens). AOX is that part of TOX that can be adsorbed to active carbon, which is the case for most DBPs. However, the composition of AOX and its relationship with ecotoxicity is unknown and may change even if absolute quantities remain equal. Therefore, there is too little

information to define an acceptable AOX-level that can be used as a trigger for environmental risk assessment that relates to ecotoxicological effects. It is recommended that (change in) AOX is investigated alongside the substance-by-substance PEC/PNEC approach for known DBPs and WET for unknowns, so that the interrelationship between these lines of evidence can be established. Other valuable descriptive parameters may be Total Organic Carbon (TOC) and total Kjeldahl nitrogen, since higher levels of these parameters generally require higher dosages of biocide.

#### 3.3.1.3 Addressing the unknown DBPs

As indicated before (see sections 1.2 and 3.2.2) a large fraction of the DBPs has not (yet) been identified and even if they would be identified, it is impossible to generate ecotoxicity data to derive PNECs for large numbers of compounds. The unknown DBPs can make up 50-60% of the total load of DBPs. In a study into the characterisation of organic halogens that result from drinking water disinfection (Reckhow et al., 2007) , chemical and physical property based measurements (i.e., resin adsorption and membrane separation) indicated that the majority of the unknown DBPs is in the mid-size range (0.5-10 kDa), but includes a wide spectrum of partitioning properties or hydrophobicities. These sizes suggest that the bulk of the unknown fraction resembles halogenated fulvic acid molecules with little fragmentation, however, substantial modification in the form of greater densities of hydrophilic groups (carboxylic acids) may occur (Reckhow et al., 2007) . Although the unknown fraction is most likely predominantly made up of sparsely-chlorinated macromolecules that are not necessarily biologically active, a clear picture of the composition of this fraction is absent. Therefore, additional testing is needed to address the potential effects of the unknown DBP fraction. For this, the concept of Whole Effluent Testing (WET) is considered to be useful. WET was originally developed for the evaluation of complex industrial effluents (see Appendix 5), which is different from biocide authorisation. Therefore, it may be necessary to combine a WET-like approach with other tailor-made experimental studies (see further 3.3.5.3) WET and other studies are thus not solely used as a higher tier test, but performed in addition to/in combination with the PEC/PNEC approach for the known DBPs. Emission of DBPs will in most cases be continuous and thus chronic exposure is expected. Results from short-term WET cannot be extrapolated to long-term test and therefore chronic exposure should also be included when considering WET. Of course, WET is only applicable to solutions. For other PTs (e.g. PT3) the primary emission will predominantly be to other compartments, e.g. manure and soil. The development of methods for the assessment of DBPs via discharge routes other than water is identified as a subject for further research.

#### 3.3.1.4 Environmental risk assessment scheme

The resulting environmental risk assessment scheme consists of three steps. The steps should not be seen as consecutive tiers, but should be completed, as required, in order to pass the risk assessment.

Step 1 Worst-case PEC/PNEC calculation for known markers assuming 100% conversion.

Step 2 Chemical assessment (descriptive group parameters).

Step 3 Refined PEC/PNEC assessment for known marker DBPs, appended with WET or other tailor-made studies to cover unknown DBPs.

Step 1 will be used to deselect the known DBPs for which no further assessment is needed, and to stop further investigation if there is no risk identified for the worst-case DBPs. If for the most toxic known DBP this step results in a PEC/PNEC <1, the less toxic ones of the known DBPs will also pass the assessment. For the known DBPs that fail step 1, a further risk assessment is needed. This can be done by refining PECs by modelling with realistic conversion factors and/or by using monitoring data or

measurements, or by refining the effects assessment by e.g. extending the dataset to allow for lower assessment factors, or by using the ecotoxicity information from the WET-approach (step 3).

Step 2 will be used to gather knowledge on how (changes in) these parameters relate to (changes in) ecotoxicity. Further knowledge on this is needed to explore the possibility of defining quantitative triggers. It may well be that this is scenario-dependent and different triggers should be set for different situations.

Step 3 is used to address the unknown DBP fraction, and may also serve to refine the risk assessment for the known DBPs.

In the next sections, specific aspects of the assessment will be discussed in more detail.

### 3.3.2 Use of existing information

In general, the efficient use of existing information is highly encouraged, and also referred to in this document where possible. Some individual DBPs are subject of authorisation as biocidal active substance (e.g. monochloramine, bromoacetic acid) or have been assessed under the former Existing Substances Regulation 793/93/EEC (e.g. sodium hypochlorite, chloracetic acid). It should be noted here that there may be legal issues associated with the use of established PNECs or other information if the underlying studies are subject to data protection (see also section 3.3.5). The rules for data protection are laid down in the BPR. If in doubt, applicants may ask their respective CAs for advice.. Moreover, changes in operating conditions and/or availability of new information may require that earlier derived PECs and/or PNECs are updated or refined.

The key-parameters that govern the nature and quantity of DBPs likely to be formed during use of an active halogen biocide are: pH, nature of the substrates present, applied dose, contact time and temperature. These factors should be evaluated to determine if a risk assessment may be extrapolated from one particular use to another.

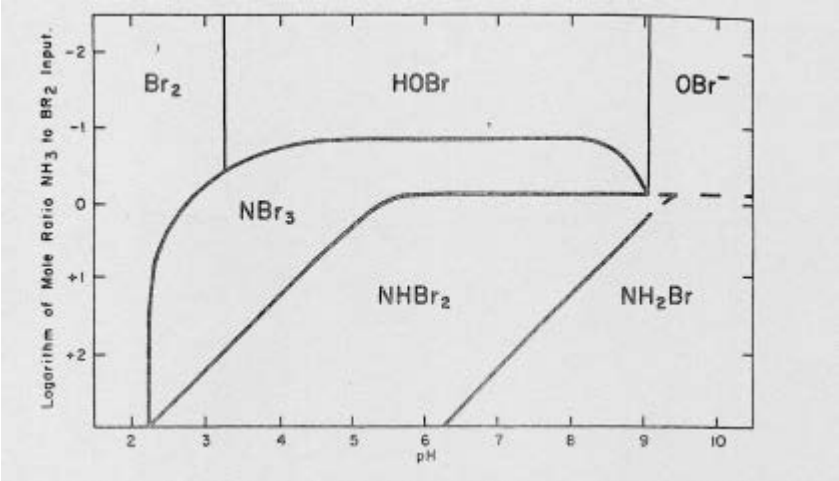
#### 3.3.2.1 Influence of pH

Regarding pH, it can be assumed that at pH 6 and higher there may be minor shifts in the relative proportions of specific by-products (for example increased THM formation as pH rises), but the overall hierarchy will not change. This means that THM will be dominant, followed by HAA, followed by haloaldehydes, haloketones and haloacetonitriles followed by minor groups. At pH >6 there is no significant formation of polyhalogenated dioxins, furans, etc.

#### 3.3.2.2 Influence of substrate

For the comparison of substrates, it is important to consider if the substrate is dominated by proteins, carbohydrates and/or fats (e.g. surface cleaning, swimming pools), or by natural organic matter (groundwater). The presence of free ammonia, amino-nitrogen or reducing inorganics (e.g. sulphides) is another point of consideration. Presence of these substrates will rapidly deplete residual oxidant and thereby limit DBP formation in general. In addition, some effect on the DBP pattern may be expected because completion of reactions (e.g. THM formation) may be reduced. Upon drinking water disinfection, ammonia is applied in combination with chlorine in order to prevent formation of trihalomethanes (Sun et al., 2009a). This will result in the formation of inorganic and organic N-chloramines, part of which will react further and may in the end also form chlorinated organics. There are scenarios in which a combination of substrates is available (e.g. sewage treatment). For treated wastewater, it has been shown that formation of halogenated organic by-products is higher in the absence of ammonia (Rebhun et al., 1997). As an illustration, Figure 4 shows the formation of different forms of brominated compounds as a function of pH and ammonia.

**Figure 4: Different forms of bromine at various pH values and various concentrations of ammonia** (figure copied from http://www.lenntech.com/)




### 3.3.2.3 Dose, contact time and temperature

An increase of the applied dose, contact time and temperature will generally lead to increased DBP formation. The extent to which this occurs depends on the (continued) presence of suitable substrates, and a threshold may quickly be reached. In real use situations, DBP formation will be limited by available substrates and will level off, which in practice means that doubling the dose will in most cases not lead to a two-fold higher DBP formation. For example, if neat rather than dilute bleach is used in cleaning, the dose may be orders of magnitude greater, but DBP formation is of a very similar order. However, a worst case extrapolation may be sufficient if no unacceptable risk is predicted. The influence of temperature is more complex, but there is some evidence from the use of bleach in laundry that a doubling in DBP formation with every 10 °C increase would be a worst case assumption (personal communication John Pickup, Global net).

### 3.3.2.4 Other relevant parameters

Other parameters may be useful to evaluate the similarity between scenarios. For chlorine, these include:

- Chlorine to carbon ratio: at low ratios, active chlorine concentrations diminish and may disappear, the rate depending on the substrate);
- Presence of 'free available chlorine': establishment of a residual generally means that the initial oxidant demand has been satisfied; prolonged presence of residuals will allow for completion of slower reactions and a change in DBP-pattern. In general an application with residual chlorine would be worst case as compared to one without residual present.
- Balance of halogen present: in most situations, chlorine dominates versus brominated and iodinated compounds and chlorinated organics similarly dominate the by-products. However, where bromide concentrations are high, brominated organics generally dominate.

When evaluating the relevance of an existing risk assessment for a new situation, the above mentioned key-parameters (pH, substrate, dose, contact time and temperature) should be included in the argumentation, and their impact on formation of the known DBPs that should be addressed in the risk assessment (see 3.3) should be evaluated. Appendix 2 includes examples on the comparison of use scenarios for hypochlorite based on the EU-RAR.

### 3.3.3 Known DBPs to be included in the assessment

#### 3.3.3.1 Relevant DBP-groups and their representatives

The DBP-groups that should be addressed in the environmental risk assessment of halogenated oxidative biocides in PT2, 11 and 12 are given in Table 4, together with representative compounds within each group. The selection is based on expert information on the principal groups of DBPs (see also section 3.2.2). As stated in the previous section, it is not the intention to extend Table 4 to be an endless list of DBPs. However, it is the responsibility of the applicant to address additional DBPs if there are indications that a particular biocidal use leads to formation of DBPs that are not included in Table 4. Such information may become available in the exposure assessment, e.g. from monitoring data or based on theoretical predictions (see also section 3.3.4).

**Table 4: DBPs that should be addressed in the environmental risk assessment of oxidative halogenated biocides. The relevant individual chlorinated and brominated forms are listed where applicable.**

| DBP | Relevant representative compounds |
|---|---|
| Trihalomethanes (THMs) | trichloromethane (chloroform)<br>tribromomethane (bromoform)<br>dichlorobromomethane<br>dibromochloromethane |
| Halogenated acetic acids (HAAs) | monochloroacetic acid (MCA)<br>dichloroacetic acid (DCA)<br>trichloroacetic acid (TCA)<br>monobromoacetic acid (MBA)<br>dibromoacetic acid (DBA)<br>tribromoacetic acid (TBA)<br>bromodichloroacetic acid<br>dibromochloroacetic acid<br>bromochloroacetic acid |
| Halogenated acetonitriles (HANs) | dichloroacetonitrile<br>trichloroacetonitrile<br>chlorobromoacetonitrile<br>dibromoacetonitrile |
| Bromate | - |
| Halogenated phenols | case-by-case assessment |
| Halogenated amines | case-by-case assessment |

In principle all individual compounds of the DBP-groups should be addressed in the risk assessment, but in some cases a group assessment may be appropriate (see further section 3.3.5.2). Specific compounds may be excluded based on argumentation (e.g. if they are not formed under specific conditions). Bromate may be formed upon chlorination of bromide-containing water. This is the case for seawater, but bromate formation can also be relevant for inland waters that contain relatively high levels of bromide. Regarding halogenated amines it is noted that section 3.2.2.9 refers to the fact that breakpoint chlorination may cause partial degradation of these DBPs. Whether breakpoint chlorination occurs and whether halogenated amines are indeed degraded should be taken into consideration in the specific risk assessment. Halogenated phenols

are also group to consider case-by-case because they are formed probably only in trace amounts.

### 3.3.4 Exposure assessment

#### 3.3.4.1 Relevant compartments

The biocidal active substances that are under evaluation in PT2, 11 and 12 are mainly discharged to water. For other PTs (e.g. PT3) the primary emission will predominantly be to other (intermediate) compartments, e.g. manure and soil. For cooling towers (and STPs), emission of haloforms to air should be taken into account. In principle, all potentially relevant environmental compartments should be addressed in the DBP-assessment. The assessment of DBPs should basically follow that for the active substance. Including relevant scenarios at the stage of active substance approval will facilitate mutual recognition of products at a later stage. Depending on the proposed use and the characteristics of the compound, sediment, air, soil, groundwater and biota (secondary poisoning) may thus need to be included. It is noted that the known DBPs selected in section 3.3.3 are mainly soluble compounds for which soil, sediment and biota are probably not the primary compartment of concern in view of their environmental behaviour. In addition, knowledge on the exposure and effects related to these latter compartments may be limited as compared to surface water. Although it is recognised that it may be not feasible to perform a full quantitative risk assessment, all relevant compartments should be addressed, making use of existing information as much as possible.

#### 3.3.4.2 Exposure assessment strategies

As indicated in section 3.3.1, as a worst case approach the PEC of a DBP can be derived from the PEC of the active substance assuming 100% conversion of the active substance. If a potential risk is identified, a refined exposure assessment should be performed. This can be done by (a combination of) modelling and monitoring approaches. Monitoring in this context does not (only) refer to extended time series over several locations, but also includes “measurements” that relate to more or less project-based sampling campaigns, limited in scale with respect to time and place.

##### 2.3.4.2.1 Existing monitoring data

Existing monitoring data can be used if it can be shown that conditions under which they were gathered still apply. This would be the case for those PTs where there have not been many process changes over time. For this, the key parameters listed in section 3.3.2 should be carefully evaluated. In this respect, it is concluded that the monitoring data on DBP-formation in cooling water systems that were published in the late 1990’s (Berbee, 1997; Jenner et al., 1997; Khalanski, 2002) and summarised in the EU-RAR on sodium hypochlorite (EC, 2007), are still applicable to the current situation (for details see Appendix 2). For other PTs, it is not possible at this stage to draw such a generalised conclusion and applicants should provide a justification that existing information may be used and relied on.

##### 2.3.4.2.2 Generating new data

There may be cases in which applicants wish to generate new measurements. It is recognised that the design of field sampling campaigns and evaluation of monitoring data is a complex issue which is outside the scope of this document. Valuable information on this topic can be found in existing guidance (ECHA, 2012; OECD 2000; 2013). However, monitoring requirements for DBPs cannot be more stringent than currently applied for active substances for which the risk assessment is almost always based on exposure modelling. When measured concentrations of DBPs are used, it should be clear that they originate from the biocide treatment which is subject of authorisation. In some cases, information may be obtained by measuring before and after (a switch in) biocide

application. However, for PTs with indirect discharge to the municipal STP it will hardly be possible to link measured concentrations of DBPs in the STP-effluent to a particular biocidal use because different waste streams are combined in the STP. As an alternative, concentrations of DBPs may be measured at the location of use or initial discharge (e.g. in a household sewer system) and combined with fate modelling to estimate concentrations leaving the STP. It should be noted that the potential formation of additional DBPs in the municipal STP is then not taken into account, but at this stage there is no option to solve this, other than by an experimental approach.

2.3.4.2.3 Simulation and modelling studies

If monitoring or measurement data are not available or not accessible, and generation of data is not feasible, simulation and modelling studies can be used to fill in data gaps and derive realistic worst case formation percentages. Such an approach should be part of a robust argumentation and a full rationale should be given in the case of extrapolating data from one situation to another. Again, the key parameters listed in section 3.3.2 should be examined. It is advised that accepted environmental fate models or risk assessment tools (e.g. SimpleTreat, EUSES) are used where possible. In general it can be stated that on-site sampling may be appropriate in case authorisation involves one particular use type, but applying a tailor made test might be more cost efficient if several product types can be addressed in a single experiment.

## 3.3.5 Effects assessment

### 3.3.5.1 Derivation of PNECs

PNECs should be derived for the relevant known DBPs (see section 3.3.3.1). From a scientific point of view, the ecotoxicological assessment of DBPs should follow the procedures as agreed for the active substances. Existing evaluations that are performed in other (regulatory) frameworks may be a valuable source of information on data availability, but PNECs or comparable risk indicators should not be taken over without a thorough review of the underlying data. This means that industry parties should collect the relevant up-to-date data from original study reports and open literature, and prepare a summary and evaluation with respect to scientific reliability and relevance of the data for PNEC-derivation. Using the reliable and relevant data, the PNEC should then be derived according to the existing guidance under the BPR. It is acknowledged that a full dossier is probably not needed if no risk is identified already on the basis of a small dataset (and consequently large assessment factors). If the PEC/PNEC approaches 1, refinement and better underpinning of PNECs becomes necessary. To fill in data gaps, Quantitative Structure-Activity Relationships (QSARs) and/or read-across may be used according to existing guidance. The applicability of QSARs to specific DBPs (groups) should be checked relative to the individual ecotoxicity data that are available.

Most compounds that should be addressed in the risk assessment (see section 3.3.3.1, Table 4) are relevant for several active substances and/or applicants. For a consistent approach, it is advised that industry parties collectively build PNEC dossiers that are evaluated by the responsible eCAs and agreed upon by ECHA's Biocidal Products Committee (BPC). It is noted that this preparation of PNEC-dossiers requires coordination with respect to timing. In addition, the issue of data ownership should be considered. As indicated in section 3.3.3.1, it may be possible that a particular biocidal use leads to formation of DBPs that are not yet addressed in Table 1. If this is the case, it should be evaluated if the DBPs under consideration may also be relevant for other active substances and/or applicants and preparation of a collective dossier should be considered.

#### 3.3.5.2 Group ecotoxicity assessment

In some cases a group assessment may be appropriate. In the EU-RAR on sodium hypochlorite, the PNEC for chloroform was used to assess the risks of the group of THMs (EC, 2007) , arguing that chloroform is more toxic than the other components (see Appendix 2 for a summary of the EU-RAR assessment on this aspect). If it can be substantiated with data that one particular component is indeed most toxic, comparing the PNEC of this compound with the summed PEC of all components represents a worst case approach. However, this approach may be too stringent when the PNEC of the most toxic compound is much lower than that of the others, but this compound represents only a minor fraction of the total. The choice to perform a risk assessment for a DBP-group on the basis of a selected (set of) compound(s) should be justified by an evaluation of the ecotoxicity data for the individual chlorinated and brominated compounds and their contribution to the total exposure.

#### 3.3.5.3 Whole Effluent Testing (WET)

According to the procedure presented in section 3.3.3.13, WET is applied to address the potential risks of unidentified DBPs and/or DBPs for which no information on ecotoxicity is available. As indicated before, the general WET-approach was developed for the evaluation of complex industrial effluents, and may be adapted for biocide authorisation. For the latter, the potential effects related to a specified use of a particular biocide have to be evaluated. An option could be to compare the ecotoxicity of effluents before and after treatment. However, this strategy cannot be used when actual operating conditions involve continuous treatment (Baltus et al., 1999). Furthermore, when using WET for actual effluents, the potential effects of the active substance itself often cannot be disentangled from those resulting from DBP-formation. Moreover, different (biocide) disinfection treatments may be applied simultaneously or in succession under normal operating conditions, so that it may be difficult to relate observed effects to one particular biocide. Because of these practical problems, it may be worthwhile to consider a WET-like approach in a simulation study that covers the proposed use with respect to the range and concentrations of DBPs to be expected. This approach was applied when addressing the potential effects of DBPs resulting from sewage chlorination (see Appendix 6, A6 2.3). Any WET or additional test should be fit for purpose and it should be made clear to which situations (process conditions, wastewater characteristics, biocides used, etc.) a particular test is applicable. This information is crucial to decide if results can be extrapolated to other situations.

The interpretation of WET in terms of acceptability of effects may be difficult. The usual approach is to classify effluents according to the dilution or concentration rate which is needed to reach a certain effect level in a bioassay. As for the “normal” ecotoxicity endpoints, it has to be decided which dilution is acceptable, i.e. which dilution level is considered equivalent to the NOEC or EC10. Although assessment criteria have been proposed or established in some countries (see Appendix 5 for more details), an acceptable dilution level has not been discussed or agreed upon yet in the context of biocide authorisation. The evaluation of the WET-results should thus be done on a case-by-case basis. It should be kept in mind that the purpose of the assessment is to evaluate the effects of the DBPs. In that respect it can be argued that it is not needed to show that there are no effects at all, but that the contribution of DBPs to the effects is negligible. Therefore, WET can also be applied to demonstrate that no changes in effects are observed when comparing samples with and without DBPs. An example of such a comparative approach can be found in the summary of the EU-RAR in Appendix 6 (see A6 1.2).

### 3.3.6 Mixture toxicity

According to existing guidance under the BPR simultaneous exposure should be taken into account in the assessment of biocides. The guidance should in principle be followed and the available data should be used to explore the mixture toxicity approach. However, at present there is probably much uncertainty on the individual PNECs, in particular when an initial assessment is performed based on a limited dataset. Furthermore, some DBPs may be assessed as a group, thus already including the mixture effects within a group. Also the WET-approach addresses the combined ecotoxicity of all compounds together. Therefore, mixture toxicity should be addressed in the risk assessment, but the uncertainties of the mixture toxicity approach should be expressed on a case by case basis.

### 3.3.7 Relevance of other PTs

The present guidance is developed in view of the assessment of biocides in PT2, 11 and 12, but the environmental risk assessment of DBPs may be relevant for other PTs as well. To focus future work, the workshop participants were asked to indicate for which PTs an environmental risk assessment of DBPs would be necessary. The resulting list is presented below. From this inventory, it appears that PTs 1, 3, 4 and 5 are considered most relevant from the perspective of environmental risks of DBPs. Please note that this is a tentative list since only few responses were received. Also note that relevance in this context is related to potential DBP-formation and emission as a direct result of the use of halogenated oxidising biocidal active substances in a particular PT. It is recognised that many processes operate on potable water. Potable water may contain DBPs due to prior disinfection, but these are not considered to be associated with the biocide itself. Where the present framework is primarily focused on discharge to surface water, these PTs may comprise other emission routes, e.g. manure and soil in PT3. Although the basic principles of the risk assessment strategy for known DBPs can be applied, it will be a challenge to estimate exposure and to translate the WET-approach for unknown DBPs to other compartments (see also section 3.3.4.1).

**Table 5: Potential relevance of PTs regarding the environmental risk assessment of DBPs in the context of biocides authorisation.**

| PT | Description of use area and products | Relevance for ENV | Argumentation |
|---|---|---|---|
| PT 1: Human hygiene | Products in this group are biocidal products used for human hygiene purposes, applied on or in contact with human skin or scalps for the primary purpose of disinfecting the skin or scalp. | Yes | There is a specific use-pattern in PT1 for hand- and foot- disinfection directly using active chlorine solution.. Iodinated products may also be used, the mode of action of these is different. |
| PT 2: Disinfectants and algaecides not intended for direct application to humans or animals | Products used for the disinfection of surfaces, materials, equipment and furniture which are not used for direct contact with food or feeding stuffs. | Yes | Surface cleaning may be carried out with halogenated oxidants in both consumer and industrial sectors. This includes but is not limited to toilets and sinks. |

| PT | Description of use area and products | Relevance for ENV | Argumentation |
|---|---|---|---|
| | Usage areas include, inter alia, swimming pools, aquariums, bathing and other waters; air conditioning systems; and walls and floors in private, public, and industrial areas and in other areas for professional activities. | Yes | Products are widely used in private swimming pools, direct emissions hard to prevent. |
| | Products used for disinfection of air, water not used for human or animal consumption, chemical toilets, waste water, hospital waste and soil. | Yes | Disinfection of waste water is a potentially large source of DBP formation |
| | Products used as algaecides for treatment of swimming pools, aquariums and other waters and for remedial treatment of construction materials. | Yes | already covered above |
| | Products used to be incorporated in textiles, tissues, masks, paints and other articles or materials with the purpose of producing treated articles with disinfecting properties. | No | Halogenated biocidal actives not considered suitable for these scenarios, as the quality of the products would be reduced. |
| PT 3: Veterinary hygiene | Products used for veterinary hygiene purposes such as disinfectants, disinfecting soaps, oral or corporal hygiene products or with anti-microbial function. | Yes | Treatment of large surfaces, discharge of waste water via manure storage |
| | Products used to disinfect the materials and surfaces associated with the housing or transportation of animals. | Yes | |
| PT 4: Food and feed area | Products used for the disinfection of equipment, containers, consumption utensils, surfaces or pipework associated with the production, transport, storage or consumption of food or feed (including drinking water) for humans and animals. | Yes | Large scale use of products for disinfection of pipework in e.g. breweries or stables. |

| PT | Description of use area and products | Relevance for ENV | Argumentation |
|---|---|---|---|
| | Products used to impregnate materials which may enter into contact with food. | No | Not expected to include halogenated oxidising active substances. |
| PT 5: Drinking water | Products used for the disinfection of drinking water for both humans and animals | Yes | Tap water is used for all kinds of other purposes (cleaning, showering) and will be released to the environment either directly or indirectly. |
| PT6: Preservatives for products during storage | Products used for the preservation of manufactured products, other than foodstuffs, feedingstuffs, cosmetics or medicinal products or medical devices by the control of microbial deterioration to ensure their shelf life.<br>Products used as preservatives for the storage or use of rodenticide, insecticide or other baits. | No | Not expected to include halogenated oxidising active substances. |
| PT7: Film preservatives | Products used for the preservation of films or coatings by the control of microbial deterioration or algal growth in order to protect the initial properties of the surface of materials or objects such as paints, plastics, sealants, wall adhesives, binders, papers, art works. | No | Not expected to include halogenated oxidising active substances. |
| PT 8: Wood preservatives | Products used for the preservation of wood, from and including the saw-mill stage, or wood products by the control of wood-destroying or wood-disfiguring organisms, including insects. This product-type includes both preventive and curative products. | No | Not expected to include halogenated oxidising active substances. |
| PT 9: Fibre, leather, rubber and polymerised materials preservatives | Products used for the preservation of fibrous or polymerised materials, such as leather, rubber or paper or textile products by the control of microbiological | No | Not expected to include halogenated oxidising active substances. |

| PT | Description of use area and products | Relevance for ENV | Argumentation |
|---|---|---|---|
| | deterioration.<br>This product-type includes biocidal products which antagonise the settlement of micro-organisms on the surface of materials and therefore hamper or prevent the development of odour and/or offer other kinds of benefits. | | |
| PT 10: Construction material preservatives | Products used for the preservation of masonry, composite materials, or other construction materials other than wood by the control of microbiological, and algal attack. | No | Not expected to include halogenated oxidising active substances. |
| PT 11: Preservatives for liquid-cooling and processing systems | Products used for the preservation of water or other liquids used in cooling and processing systems by the control of harmful organisms such as microbes, algae and mussels. Products used for the disinfection of drinking water or of water for swimming pools are not included in this product-type. | Yes | Potentially large direct emissions in once-through systems. Also relevant for recirculating systems. |
| PT 12: Slimicides | Products used for the prevention or control of slime growth on materials, equipment and structures, used in industrial processes, e.g. on wood and paper pulp, porous sand strata in oil extraction. | Yes | Large potential for DBP formation because of presence of suitable substrate. |
| PT 13: Working or cutting fluid preservatives | Products to control microbial deterioration in fluids used for working or cutting metal, glass or other materials. | No | Not expected to include halogenated oxidising active substances. |
| PT14-20 pest control | | No | Not expected to be disinfectants and/or to include halogenated oxidising active substances. |
| PT21: | Products used to control the | No | Not expected to include |

| PT | Description of use area and products | Relevance for ENV | Argumentation |
|---|---|---|---|
| antifouling | growth and settlement of fouling organisms (microbes and higher forms of plant or animal species) on vessels, aquaculture equipment or other structures used in water. | | halogenated oxidising active substances. |
| PT 22: Embalming and taxidermist fluids | Products used for the disinfection and preservation of human or animal corpses, or parts thereof. | No | Not expected to include halogenated oxidising active substances. |

## 3.4 Conclusions and Recommendations

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. The approach should be part of a robust argumentation and a full rationale should be given in the case of extrapolating data from one situation to another. Most compounds that should be addressed in the risk assessment are relevant for several active substances and/or applicants. It is recommended that, industry parties coordinate activities and jointly prepare PNEC-dossiers according to the existing guidance. WET or similar additional dedicated tests should be applied for the effects assessment of the unknown DBPs and may also be used to refine the risk assessment of the known marker DBPs. Existing information should be used where possible, but the applicability to the present situation should be demonstrated. It is recommended that the responsible authorities takes action to remove legal or procedural obstacles regarding the use of information from other assessments.

The present guidance focuses on PT2, PT11 and PT12 for which environmental exposure was considered most relevant in view of the extent of DBP formation in combination with

emissions to surface water. There are uncertainties as to whether the selected marker DBPs are representative for other compartments than surface water. The uncertainties related to potential risks for sediment, soil and biota as well as those related to mixture toxicity should be discussed in the risk assessment. Other PTs for which a DBP-assessment may be needed are PT1, 3, 4 and 5. It is recommended to further investigate the applicability of the present guidance to these PTs.

# 4. References

**NOTE to the reader:**

Reference list includes references used in the Appendices

ANSES. 2012. Évaluation des risques sanitaires liés aux piscines. Mars 2012. Édition scientifique. http://nosobase.chu-lyon.fr/recommandations/anses/2010_piscine_anses_maj2012.pdf (Accessed August 2015).

Baltus CAM, Kerkum LCM, Kienhuis PGM. 1999. Acute toxiciteit van koelwaterlozingen uit recirculatiekoelsystemen. Resultaten van veld- en laboratoriumonderzoek. Lelystad, the Netherlands. RIZA. Report nr. 99.025.

Bengtsson B-E, Breitholtz M, Eklund B, Viktor T. 2009. Utvärdering av biologiska tester gjorda på svenska skogsindustriavlopp 2001-2007. Bromma, Sweden. Naturvårdsverket. Report nr. 6304.

Berbee RPM. 1997. Hoe om te gaan met actief chloor in koelwater? Lelystad, the Netherlands. RIZA. Report nr. 97.077.

Cardador MJ, Gallego M. 2011. Haloacetic acids in swimming pools: swimmer and worker exposure. Environ Sci Technol 45, 5783-5790.

Chrobok K. 2003. Desinfektionsverfahren in der Schwimmbeckenwasseraufbereitung unter besondere Berücksichtigung des elektrochemischen Aktivierungsverfahren zwecks Verbesserung der Beckenswasserqualität. Dissertation im Fachbereich der Biologie – Universität Bremen. Dezember 2003.

Davis R, Holmes D, Horn K, Hutchison J, Lunt D, Tynan P. 1993. Wastewater disinfection – Laboratory/Field Studies. Medmenham, Marlow, Bucks, UK. WRc. Report nr. R&D Note 218.

DeBorde M, Von Gunten U. 2008. Reactions of chlorine with inorganic and organic compounds during water treatment - Kinetics and mechanisms: a critical review. Wat Res 42, 13-51.

Dygutsch DP, Kramer M. 2012. Chlorit und Chlorat - Ein neuer Summenparameter der DIN19643 zur Überwachung von Schwimmbeckenwasser. Wasseraufbereitung - Bädertechnik AB Archiv des Badewesens 03/2012 166.

EC. 1998. COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF.

EC. 2007. European Union Risk Assessment Report SODIUM HYPOCHLORITE, CAS No: 7681-52-9, EINECS No: 231-668-3, Final report, November 2007. Rapporteur Member State Italy, http://esis.jrc.ec.europa.eu/doc/existing-chemicals/risk_assessment/REPORT/sodiumhypochloritereport045.pdf.

ECHA. 2012. Guidance on information requirements and chemical safety assessment Chapter R.16: Environmental Exposure Estimation. Helsinki, Finland. European Chemicals Agency.

Erdinger L, Kirsch F, Sonntag HG. 1999. Chlorate as an inorganic disinfection by product in swimming pools. Zentralblatt für Hygiene und Umweltmedizin 202, 61-75.

EU. 1998. COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. European Commission http://eur-

lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF (Accessed August 2015)

EU (2008) European Risk Assessment Report – Chloroform. Draft of May 2008. http://echa.europa.eu/documents/10162/13630/trd_rar_hh_france_chloroform_en.pdf (Accessed August 2015)

Fantuzzi G, Righi E, Predieri G, Giacobazzi P, Petra B, Aggazzotti G. 2013. Airborne trichloramine (NCl3) levels and self-reported health symptoms in indoor swimming pool workers: dose-response relationships. J Expo Sci Environ Epidemiol 23, 88 – 93

FEI. 2010. COHIBA. Control of hazardous substance in the Baltic Sea region. Whole effluent assessment (WEA). Proposed recommendations for the use of toxicity limits. Helsinki, Finland. Finnish Environment Institute SYKE.

Hernando MD, Fernandez-Alba AR, Tauler R, Barcelo D. 2005. Toxicity assays applied to wastewater treatment. Talanta 65, 358-366.

Hery M, Hecht G, Gerber JM, Gendre JC, Hubert G, Rebuffaud J. 1995 Exposure to chloramines in the atmosphere of indoor swimming pools. Ann Occup Hyg 39:427–9.

HSDB. 2012. Hazardous Substances Database. Accessed March 2012.

INRS. 2015. Triklorame, kit de mesure de la trichloramine dans l'air. http://www.inrs.fr/services/innovation/evaluation-diagnostic/triklorame.html (Accessed August 2015)

Jacobs JH, Spaan S, Van Rooy GBGJ, Meliefste C, Zaat VAC, Rooyackers JM, Heederik D. 2007. Exposure to trichloramine and respiratory symptoms in indoor swimming pool workers. Eur Respir J 29, 690-698.

Jenner HA, Taylor CJL, Van Donk M, Khalanski M. 1997. Chlorination by-products in chlorinated cooling water of some European coastal power stations. Mar Environ Res 43, 279-293.

Jin W, Zhou J, Chen B, Zhu X, Cui C. 2012 Modeling volatilization and adsorption of disinfection byproducts in natural watersheds. J Environ Monit, 14, 2990-2999.

Jolley RL, Cumming RB, Lee NE, Thompson JE, Lewis LR. 1982. Micropollutants produced by disinfection of wastewater effluents. Wat Sci Tech 14, 45-59.

Kaman A. 2010. Occurrence and formation of disinfection by-products in indoor swimming-pools water. Dissertation Graduate School Clemson University.

Khalanski M. 2002. Organic by-products generated by the chlorination of cooling water at EDF marine power stations: Electricité de France. Report nr. R&D Report HP-75/2002/026/A.

Krassner SW, Weinberg HS, Richardson SD, Pastor SJ. 2006. Occurrence of a new generation of disinfection byproducts. Environ Sc Technol 40, 7175-7185.

Lee J, Jun MJ, Lee MH, Lee MH, Eom SW, Zoh KD. 2010. Production of various disinfection byproducts in indoor swimming pool waters treated with different disinfection methods. Int J Hyg Environ Health 213, 465-474.

Lilja K, Remberger M, Kaj L, Allard A-S, Andersson A, Broström-Lundén E. 2010. Chemical and biological monitoring of sewage effluent water. Stockholm, Sweden. IVL Swedish Environmental Research Institute Ltd. . Report nr. B1897.

Maas JH, Van de Plassche EJ, Straetmans A, Vethaak AD, Belfroid AC. 2003. Normstelling voor bioassays. Uitwerking voor oppervlaktewater en waterbodems. Lelystad, the Netherlands. RIZA. Report nr. 2003.005.

Massin N, Bohadana AB, Wild P, Héry M, Toamain JP, Hubert G. 1998. Respiratory symptoms and bronchial responsiveness in lifeguards exposed to nitrogen trichloride in indoor swimming pools. Occup Environ Med 55, 258-263.

Mendonca E, Picado A, Paixão SM, Silva L, Cunha MA, Leitão S, Moura I, Cortez C, Brito F. 2009. Ecotoxicity tests in the environmental analysis of wastewater treatment plants: Case study in Portugal. J Hazard Mat 163, 665-670.

Meric S, De Nicola E, Iaccarino M, Gallo M, Di Gennaro A, Morrone G, Warnau M, Belgiorno V, Pagano G. 2005. Toxicity of leather tanning wastewater effluents in sea urchin early development and in marine microalgae. Chemosphere 61, 208-217.

Mhlongo S, Mamba BB, Krause RW. 2009. Nitrosamines: A review on their prevalence as emerging pollutants and potential remediation options. Water SA 35, 735-740.

Naturvårdsverket. 2011. Kemisk och biologisk karakterisering av punktutsläpp till vatten. En handbok med vägledning om bestämning av egenskaperna hos utsläpp av avloppsvatten (Handbook for chemical and biological characterisation of point emissions to water). Stockholm, Sweden. Naturvårdsverket. Report nr. Handbok 2010:3.

Nordberg GF, Lundstrom NG, Forsberg B, Hagenbjork-Gustafsson A, Lagerkvist BJ, Nilsson J, Svensson M, Blomberg A, Nilsson L, Bernard A, Dumont X, Bertilsson H, Eriksson K. 2012 Lung function in volunteers before and after exposure to trichloramine in indoor pool environments and asthma in a cohort of pool workers. BMJ Open 2:e000973

OECD. 2000. Report of the OECD Workshop on Improving the Use of Monitoring Data in the Exposure Assessment of Industrial Chemicals. OECD SERIES ON TESTING AND ASSESSMENT. Number 18. Available via http://www.oecd.org/chemicalsafety/testing/seriesontestingandassessmentemissionandexposure.htm.

OECD. 2013. Guidance document for exposure assessment based on environmental monitoring. OECD Series on Testing and Assessment. No. 185. Available via http://www.oecd.org/chemicalsafety/testing/seriesontestingandassessmentemissionandexposure.htm.

Oral R, Meriç S, De Nicola E, Petruzzelli D, Della Rocca C, Pagano G. 2007. Multi-species toxicity evaluation of a chromium-based leather tannery wastewater. Desalination 211, 48-57.

OSPAR. 2005. Hazardous Substances Series. Whole Effluent Assessment 2005/219.

Parinet J, Tabaries S, Coulomb B, Vassalo L, Boudenne J-L. 2012 Exposure levels to brominated compounds in seawater swimming pools treated with chlorine. Wat Res 46, 828-836.

Parrat J, Donze G, Iseli C, Perret D, Tomici C, Schenk O.2012. Assessment of occupational and public exposure to trichloramine in swiss indoor swimming pools: A proposal for an occupational exposure limit. Ann Occup Hyg 56, 1-14.

Pickup J. 2010Environmental safety of halogenated by-products from use of active chlorine. Brussels, Belgium. Euro Chlor. Report nr. Science Dossier 15.

Plewa MJ, Muellner MG, Richardson SD, Fasano F, Buettner KM, Woo Y-T, McKague AB, Wagner ED. 2008. Occurrence, synthesis, and mammalian cell cytotoxicity and genotoxicity of haloacetamides: An emerging class of nitrogenous drinking water disinfection byproducts. Environ Sci Technol 42, 955-961.

Pool Water Treatment bv. 2014. Kosteneffecten kwaliteitseisen (water en lucht) in de voorgestelde herziening regelgeving Bhvbz. Revision, August 21 2014.

Power EA, Boumphrey RS. 2004. International trends in bioassay use for effluent management. Ecotoxicology 13, 377-398.

Pressman JG, Richardson S, Speth TH, Miltner RJ, Narotsky MG, Hunter SE, Rice GE, Teuschler LK, McDonald A, Parvez S, Krasner SW, Weinberg HS, McKague AB, Parrett CJ, Bodin N, Chinn OR, Lee C-F, Simmons JE. 2010. Concentration, chlorination, and chemical analysis of drinking water for disinfection byproduct mixtures health effects research: U.S. EPA's four lab study. Environ Sci Technol 44, 7184-7192.

PWTAG CoP 1.13. 2013 Pool Water Treatment Advisory group. Code of Practice: the management and treatment of swimming pool water. http://www.edlc.co.uk/pdf/PWTAG%20CodeofPractice1.13v5_000.pdf

Rebhun M, Heller-Grossman L, Manka J. 1997. Formation of disinfection byproducts during chlorination of secondary effluent and renovated water. Wat Environ Res 69, 1154-1162.

Reckhow DA, Hua G, Kim J, Hatcher PG, Caccamise SAL, Sachdeva R. 2007. Characterization of total organic halogen produced during disinfection processes. Denver/Washington DC, USA.

Richardson SD, DeMarini DM, Kogevinas M, Fernandez P, Marco E, Lourencetti C, Ballesté C, Heederik D, Meliefste K, McKague AB, Marcos R, Font-Ribera L, Grimalt JO, Villanueva CM. 2010. What's in the pool? A comprehensive identification of disinfection by-products and assessment of mutagenicity of chlorinated and brominated swimming pool water. Environ Health Persp 118, 1523-1530.

Richardson SD, Thruston AD, Rav-Acha C, Groisman L, Popilevsky I, Juraev O, Glezer V, McKague AB, Plewa MJ, E.D. Wagner ED. 2003. Tribromopyrrole, brominated acids and other disinfection byproducts produced by disinfection of drinking water rich in bromide. Environ Sci Technol 37, 3782–3793.

RIVM. 2014. Normen en methoden voor kwaliteitsparameters in het te wijzigen Besluit hygiëne en veiligheid badinrichtingen en zwemgelegenheden. RIVM rapport nr. 2014-0121. http://www.rivm.nl/dsresource?objectid=rivmp:279399&type=org&disposition=inline&ns_nc=1 (Accessed August 2015)

Rizzo L. 2011. Bioassays as a tool for evaluating advanced oxidation processes in water and waste water treatment. Wat Res 45, 4311-4340.

Schets FM, Schijven JF, De Roda Husman AM. 2011. Exposure assessment for swimmers in bathing waters and swimming pools. Wat Res 45, 2392-2400.

Schmalz C, Frimmel FH, Zwiener C. 2011. Trichloramine in swimming pools – Formation and mass transfer. Wat Res 45, 2681-2690.

Schmoll B, Kellner R, Breuer D. 2009. Forschungsprojekt Trichloramin in Bädern. Deutschen gestezlichen Unfallsversicherung (DGUV). Ausgabe April 2009.

Selcuk H, Eremektar G, Meric S. 2006. The effect of pre-ozone oxidation on acute toxicity and inert soluble COD fractions of a textile finishing industry wastewater. J Hazard Mat B 137, 254-260.

Selcuk H, Rizzo L, Nikolaou AN, Meric S, Belgiorno V, Bekbolet M. 2007. DBPs formation and toxicity monitoring in different origin water treated by ozone and alum/PAC coagulation. Desalination 210, 31-43.

Singh KP, Rai P, Pandey P, Sinha S. 2012. Modeling and optimization of trihalomethanes formation potential of surface water (a drinking water source) using Box–Behnken design. Environ Sci Pollut Res Int 19, 113-117.

Sun Y-X, Wu Q-Y, Hu H-Y, Tian J. 2009a. Effect of ammonia on the formation of THMs and HAAs in secondary effluent chlorination. Chemosphere 76, 631-637.

Sun Y-X, Wu Q-Y, Hu H-Y, Tian J. 2009. Effects of operating conditions on THMs and HAAs formation during wastewater chlorination. J Hazard Mater 168, 1290–1295.

Tisler T, Zagorc-Koncan J, Cotman M, Drolc A. 2004. Toxicity potential of disinfection agent in tannery wastewater. Wat Res 38, 3503-3510.

Tonkes M, De Graaf PJF, Graansma J. 1999. Assessment of complex industrial effluents in the Netherlands using a whole effluent toxicity (or WET) approach. Wat Sci Tech 39, 55-61.

Tothill IE, Turner APF. 1996. Developments in bioassay methods for toxicity testing in water treatment. Trends Anal Chem 15, 178-188.

Trabaris JM, Laskin JD, Weisel CP. 2012. Percutaneous Absorption of Haloacetonitriles and Chloral Hydrate and Simulated Human Exposures. J Appl Toxicol 32 (nr. 6): 387–394

US-EPA. 2005. Formation of bromate ion from application of dihalodialkylhydantoin sanitizers (BCDMH and DBDMH) into swimming pools and associated cancer risks for swimmers US-EPA Office of Prevention, Pesticides and Toxic Substances. Memorandum dated 8 December 2005.

US-EPA. 2010. National Pollutant Discharge Elimination System (NPDES) Permit Writers' Manual. Washington, USA. United States Environmental Protection Agency, Office of Water.

US-EPA. 2012. Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 12. http://www.epa.gov/oppt/aegl/pubs/chloroform_volume12.pdf (accessed August 2015)

VITO. 2015. Validatieverslag van de meetmethode van trichlooramine in zwembadlucht. Studie uitgevoerd in opdracht van: LNE, 2015/MRG/R/0020, Februari 2015. http://emis.vito.be/sites/emis.vito.be/files/pages/1125/2015/lucht_validatieverslag_trichlooramine_in_zwembadlucht.pdf (Accessed August 2015)

WHO (2005) Chloral Hydrate in Drinking-water- Background document for development of WHO Guidelines for Drinking-water Quality. Geneva, Switzerland. World Health Organization.

WHO. 2006. Guidelines for safe recreational water environments - Volume 2: Swimming pools and similar environments Geneva, Switzerland. World Health Organization. http://www.who.int/water_sanitation_health/bathing/bathing2/en/ (Accessed August 2015)

WHO. 2011. Guidelines for Drinking-water Quality Fourth Edition. Geneva, Switzerland. World Health Organization.

WHO. 2015. WHO Guidelines for drinking-water quality. http://www.who.int/water_sanitation_health/dwq/guidelines/en/ (Accessed August 2015)

Xu X, Mariano TM, Laskin JD and Weisel CP (2002) Percutaneous Absorption of Trihalomethanes, Haloacetic Acids, and Haloketones. Toxicology and Applied Pharmacology 184, 19–26.

Xu X, Weisel C. 2003. Inhalation exposure to haloacetic acids and haloketones during showering. Environ Sci Technol 37, 569-576.

Zhou Y, Benson JM, Irvin C, Irshad H, Cheng Y-S. 2007. Particle size distribution and inhalation dose of shower water under selected operating conditions. Inhal Toxicol 19, 333-342.

# Appendix 1. Selection of marker DBPs relevant for human exposure in swimming-water treated with halogenated disinfectants

### Trihalomethanes (THMs)

Based on the published literature on DBP formation, the trihalomethanes (THMs) is considered the most important group of DBPs both for drinking-water and for swimming-water. Of the total amount of halogenated substances in swimming-water, THMs represent about 20%, thus being the largest group of DBPs on a weight basis (Chrobok 2003). As to data on occurrence in swimming-pools THMs are by far the most data-rich group of DBPs. All four chlorinated/brominated THMs have been investigated toxicologically and national swimming-water limits are available. As the data reported by Richardson et al. (2010) clearly indicate, brominated and chlorinated DBPs are interchangeable in the sense that depending on the source levels of active chlorine or active bromine present in the treated water, formation of either the chlorinated or brominated THMs will dominate. Thus, based on existing information, THMs are a highly relevant group. Existing national THM limits for swimming-water or drinking-water apply to the sum of THMs expressed as chloroform equivalents.

Based on this THMs are selected as a marker for halogenated disinfectants for PT2. The sum concentration of all four THMs in the treated water under representative use conditions can be compared with existing THM swimming-water limits. For the appropriate existing swimming-water or drinking-water limits to be used for THMs, see section 2.4.

Due to their high volatility and Henry coefficients THMs are present in air above swimming-pools. In a summary of the literature RIVM (2014) concludes that concentrations up to 100 µg/m$^3$ occur in indoor swimming-pools with even higher concentrations in some cases up to around 200 µg/m$^3$. As explained in section 2.5, the potency of THMs for inducing local toxicity in the respiratory tract is relatively limited based on current knowledge (mainly for chloroform) (US-EPA 2012, EU-RAR 2008). Thus at the THM concentrations found in air in indoor pools the risk for local effects on the respiratory tract most likely is low. Based on this priority for measuring THMs in air is judged as low.

### Bromate

Bromate ($BrO_3^-$) can be formed after ozonation of water containing bromide. When bromide-containing water is disinfected by chlorination, formation of bromate also occurs. Much of the bromate in such situations derives from the active chlorine disinfection feedstock formulation in which bromide is converted to bromate. In indoor swimming-pools in the Netherlands disinfected with chlorinated disinfectants bromate is often found (RIVM 2014). Use of brominated disinfectants also may lead to increased bromate levels in the swimming-pool water (US-EPA 2005).

Based on the known physico-chemical and biokinetic properties of bromate the dermal and inhalation routes are considered of minor importance for bromate. Expected levels of in indoor swimming-pool air are low.

Thus, bromate is a relevant DBP for swimming-water. For selection of the appropriate existing swimming-water or drinking-water limits to be used for these chemicals, see section 2.4.

### Chlorite and chlorate

Depending on which halogenated disinfectant is used, concentrations of chlorite ($ClO_2^-$) and chlorate ($ClO_3^-$) may be increased in swimming-water. Elevated concentrations of

chlorate of up to 40 mg/L were found in German swimming-pools (n=33), traceable to increased levels in the stock solution of the halogenated disinfectant (Erdinger et al. 1999). Even higher levels of up to 140 mg/L are mentioned as found in the past in certain German pools (Dygutsch and Kramer 2012). These authors report that chlorite concentrations normally will be low only, because the further conversion into chlorate will occur under influence of the active chlorine present in the swimming-pool. Because of the influence of UV-light the levels of chlorate in outdoor pools can be higher than those in indoor pools.

Based on the known physico-chemical and biokinetic properties the dermal and inhalation routes are considered of minor importance for chlorate and chlorite. Expected levels of in indoor swimming-pool air are low.

Thus, chlorite and chlorate are selected as markers for halogenated disinfectants for PT2. For selection of the appropriate existing swimming-water or drinking-water limits to be used for these chemicals, see section 2.4.

**Haloacetic acids (HAAs)**

As indicated by Krassner et al. (2006) the haloacetic acids (chlorinated, brominated) represent the second largest group within the whole DBP mixture. The presence of HAAs in swimming-water has been shown both indoors and outdoors (Cardador and Gallego 2011). These investigators found that of the chlorinated haloacetic acids, the levels of di- and trichloroacetic acids were higher than those for monoacetic acid. For bromoacetic acids in swimming-water, recent data for eight health-oriented swimming pools (thalassotherapy establishments) based on seawater (seawater contains increased levels of bromide) are available (Parinet et al. 2012). The pools were disinfected by chlorination. For nine HAAs (three chlorinated, three brominated, three mixed bromo/chloro) they report sum levels of median 419 µg/L with a maximum of 2233 µg/L. Of the individual HAAs, highest concentrations were present of monobromoacetic acid, dibromoacetic acid, tribromoacetic acid and dibromochloroacetic acid (Parinet et al. 2012).

Based on their known physico-chemical and biokinetic properties the dermal and inhalation routes are considered not relevant for the HAAs. Expected levels of HAAs in indoor swimming-pool air are low.

Based on the above, HAAs are selected as a marker for halogenated disinfectants for PT2. For selection of the appropriate existing swimming-water or drinking-water limits to be used for this group, see section 2.4.

**Haloacetonitriles**

Haloacetonitriles constitute only 5% or less of the total DBPs after chlorination. Levels of haloacetonitriles in 23 chlorinated indoor swimming-pools in the USA ranged from 5 to 53 µg/L (mean 19 µg/L) (Kaman 2010). Dichloroacetonitrile was by far the dominant haloacetonitrile found. Levels of dibromoacetonitrile may be increased when seawater is used for swimming-pools with levels up to 49 µg/L having been reported (WHO 2006). This is due to presence of bromide in seawater. No information is available for the occurrence of haloacetonitriles in air in indoor swimming-pools. Expected air concentrations are low based on a Henry coefficient of 0.04 $Pa.m^3/mol$ (HSDB 2012).

Based on this limited information dihaloacetonitriles are selected as relevant DBPs for halogenated disinfectants of PT2. For selection of the existing swimming-water or drinking-water limits to be used for this group, see section 2.4.

**Haloaldehydes**

The only representative from this group for which there are substantial data is chloral hydrate (trichloroacetaldehyde). For bromal hydrate the only relevant piece of information is the reporting by WHO (2006) of a level of 230 µg/L for a swimming-pool

prepared from seawater. For chloral hydrate concentrations of 5-34.9 µg/L were found in 86 swimming pools in Seoul, South-Korea (Lee et al. 2010). Chloral hydrate in drinking-water is usually present at concentrations below 10 µg/L (WHO 2005). No information is available for the occurrence of bromal or chloral hydrate in air in indoor swimming-pools. Based on an estimated Henry coefficient of 0.0057 Pa.m$^3$/mol (EPIWIN) for chloral hydrate emission to air in swimming-pools, however, is expected to be low.

Based on this limited information the trihaloacetaldehydes (chloral hydrate and bromal hydrate) are selected as potentially relevant DBPs for halogenated disinfectants of PT2. For selection of the existing swimming-water or drinking-water limits to be used for this group, see section 2.4. No evaluation for possible local toxic effects in the respiratory tract is needed for this group of DBPs.

**Haloamines**

Chlorine and bromine react readily with ammonia from urine to form chloramines and bromamines respectively. In fact monochloramine is used for secondary disinfection of drinking-water (longer-lasting water treatment as the water moves through pipes to consumers) by adding ammonia downstream to water containing some residual active chlorine. In swimming-water urine is a direct source for ammonia but further ammonia can also be formed from urea present in urine. Thus after use of halogenated disinfectants in swimming-pools formation of haloamines is to be expected in principle.

Of the three chloramines, monochloramine is the dominant one at the normal pH-range (7-9) for drinking-water. When used as a disinfectant monochloramine is present at concentrations of 0.5 to 2.5 mg/L. According to WHO (2011), di- and trichloramines are formed in drinking-water only occasionally and cause taste and odour problem at lower concentrations than does monochloramine.

In swimming-water the levels of chloramines (and bromamines) formed will depend on the level of human contamination. In a study into formation of chloramines in swimming-pools in a laboratory experiment, preferable formation of trichloramine over mono- and dichloramine was found (Schmalz et al. 2011). Release of trichloramine to air took place relatively slowly (mass transfer took 20 hours in rough-surface water). Mean levels of mono-, di- and trichloramines in swimming-pool water of 290 µg/L (mono), 380 µg/L (di) and <100 µg/L (tri) are reported for a chlorinated pool in Spain (Richardson et al. 2010). Measurements carried out in Germany and Switzerland and reported in 2009 and 2012 respectively, showed significantly lower levels of trichloroamine, i.e. clearly below 500 µg/L for almost all swimming-pools (Schmoll et al. 2009; Parrat et al. 2012). Levels of trichloramine in air in chlorinated indoor swimming-pools in the Netherlands are in the range of 130-1280 µg/m$^3$ (Jacobs et al. 2007). Hery et al. (1995) and Massin et al. (1998) reported similar levels for indoor swimming-pools in France but ANSES (2012) reports a somewhat lower range for French indoor pools for the later period of 2007-2009, i.e. 200-300 µg/m$^3$.

As reported by research groups in France, the Netherlands and Switzerland, air concentrations as measured in these countries are associated with adverse respiratory effects, primarily in pool attendants but presumably also in pool consumers.

For bromamines no concentration data are available for swimming-pools. Their formation in swimming pools after use of halogenated disinfectants seems plausible.

In conclusion only limited data are available on formation of the haloamine DBPs. The few concentration measurements in disinfected water suggest mean levels up to several hundred µg's per litre, mostly as mono- and dihaloamines. The literature indicates, however, that trihaloamines are more problematic. Concentrations in air of trichloramine have been associated with health complaints. A study by Schmalz et al. 2011) also points to trichloramine as the most important chloroamine DBP for swimming-pools. Whether

tribromamine should be regarded as similar to trichloramine in regard to its occurrence and potential health effect, is uncertain (lack of relevant data).

In conclusion, based on available data evaluation for possible local toxic effects in the respiratory tract for trihaloamines is needed. For selection of the appropriate existing air limit value to be used for trihaloamines in air, see section 2.4.

# Appendix 2. Selection of water limits for marker DBPs deemed relevant for human exposure in swimming-water treated with halogenated disinfectants

### Trihalomethanes (THMs)

The following values are available:

**Table 6: Trihalomethanes (THMs)**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Trichloromethane (chloroform) | ΣTHMs: 20 (chloroform equivalents) | Swimming-water limit Germany, FINA recommendation | Unknown, most likely based on technical feasibility |
| Tribromomethane (bromoform) | ΣTHMs: 50 (chloroform equivalents) | Swimming-water limit Netherlands | TDI for chloroform, cancer risk estimation for BDCM, based on exposure calculation oral + dermal + inhalation |
| Bromodichloromethane | | | |
| Dibromochloromethane | Alternative value: ΣTHMs: 100[8] | EU drinking-water limit (Council Directive 98/83/EC) | Unknown |

Based on the requirement that the toxicological basis for the selected value must be known the Dutch swimming-water limit of 50 µg/L (sum-concentration expressed as chloroform-equivalents) is chosen for THMs. As indicated in the table, this limit was based on an exposure calculation that took into account all three routes of exposure: oral, inhalation and dermal. According to the result of the calculation inhalation is the dominant exposure route for THMs, covering more than 80% of total exposure (RIVM 2014).

### Bromate

The following values are available:

**Table 7: Bromate**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Bromate | 2000 | Swimming-water limit Germany | TDI (based on kidney toxicity) (100% allocation to swimming-water) |
| | 100 | Swimming-water limit Netherlands | Bromate is genotoxic carcinogen, extra cancer risk level of 1. $10^{-5}$ as reference, based on exposure |

[8] In Council Directive 98/83/EC this value of 100 µg/L is indexed by Note 10: “Where possible, without compromising disinfection, MSs should strive for a lower value.”

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| | | | calculation (oral only, dermal and inhalation considered negligible) |
| | 10 | EU drinking water limit, national drinking-water limit WHO drinking-water limit | Bromate is genotoxic carcinogen, value chosen based on technical feasibility, value associated with upper bound cancer risk of $5.10^{-5}$ according to WHO based on drinking-water consumption 2 L per day |

Bromate has been widely recognized as a genotoxic carcinogen (for a summary see RIVM 2014). For genotoxic carcinogens quantitative cancer risk estimation is commonly carried out. Based on such a risk estimation the WHO and EU drinking-water limits of 10 µg/L were derived. The Dutch swimming-water limit of 100 µg/L was derived in a similar fashion, taking into account the expected exposure via swimming-water. The German swimming water limit of 2000 µg/L is based on a different assessment of the carcinogenic action by bromate. Based on the principle that swimming-pool limits take precedence over drinking-water limits and that the lowest value be chosen if more than one limit value is available, the Dutch limit of 100 µg/L is chosen for use in the present context.

**Chlorate & chlorite**

The following values are available:

**Table 8: Chlorate & chlorite**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Chlorate[9] & chlorite | 700 (chlorate) | WHO drinking-water limit | TDI (based on thyroid effect) (80% allocation to drinking-water) |
| | 700 (chlorite) | WHO drinking-water limit | TDI (based on effect on brain weight, liver weight) (80% allocation to drinking-water) |
| | 30000 (Σchlorate/ chlorite) | Swimming-water limits Germany | Based on TDI based on oxidative damage of blood cells as critical effect |
| | 30000 (Σchlorate/ chlorite) | Swimming-water limit Netherlands | Based on TDI in combination with exposure calculation (oral exposure only) |

[9] At BPC Human health Working Group meeting (WG-III May -2016), it was decided that "In the absence of data (for chlorate) , the ADI is taken over from the EFSA Panel on Contaminants in the Food Chain (Scientific Opinion on risks for public health related to the presence of chlorate in food. EFSA Journal 2015;13(6):4135,103 pp)." [see final minutes at https://echa.europa.eu/about-us/who-we-are/biocidal-products-committee/working-groups]

Based on the principle that swimming-pool limits take precedence over drinking-water limits, the value of 30000 µg/L is chosen for use in the present context.

**Haloacetic acids (HAAs)**

The following values are available:

**Table 9: Haloacetic acids (HAAs)**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Monochloroacetic acid | 20 | WHO drinking-water guideline | TDI based on spleen effect, 20% of TDI allocated to water |
| Dichloroacetic acid | 50 (provisional) | WHO drinking-water guideline | Compound is genotoxic carcinogen, value chosen based on technical feasibility, value associated with upper bound cancer risk of $1.25*10^{-5}$ |
| Trichloroacetic acid | 200 | WHO drinking-water guideline | TDI based on growth and liver effects, 20% of TDI allocated to drinking-water, drinking-water consumption 2 L per day |
| Monobromoacetic acid | 20 | Read across from monochloroacetic acid | Read across from monochloroacetic acid |
| Dibromoacetic acid | 50 (provisional) | Read across from dichloroacetic acid | Read across from dichloroacetic acid |
| Tribromoacetic acid | 200 | Read across from trichloroacetic acid | Read across from trichloroacetic acid |
| Dibromochloroacetic acid | 200 | Read across from trichloroacetic acid | Read across from trichloroacetic acid |

The HAAs have low volatility and have a low potential for skin penetration. This is confirmed by the study by Cardador and Gallego (2011). In view of this using drinking-water limits for exposure via swimming-water is considered overprotective (given that the drinking-water limits assume a water ingestion of 2 L per day). Using the calculation as developed for bromate in RIVM (2014) a swimming-water limit for the HAAs can be estimated. The calculation makes use of the formula:

$E_o = C_{water} \times IVT \times T \times 10^{-9} / BW$

Where:

$E_o$ is the oral exposure in mg/kg body weight/day (on the day of the visit to the swimming-pool)

$C_{water}$ is the concentration in swimming-water

T is the time spent in the swimming-pool in minutes (30 min for babies, 180 min for adults, 180 min for athletic swimmers)

IVT is the amount of ingested swimming-pool water in mg/minute (1000 mg/min for babies, 800 mg/min for adults, 400 mg/min for athletic swimmers)

BW is bodyweight in kg (6.2 kg for babies, 60 kg for adults and athletic swimmers)

Taking into account the number of visits to the swimming pool per year the average long-term oral exposure can be calculated and compared to the long-term toxicological reference value. In RIVM (2014) this was done separately for different swimming-pool user groups (babies, adults, swimming-athletes). The values for T and IVT the formula and the number of visits per year were derived from a study by Schets et al. (2011). Thus for babies the number of visits per year was put at 13, for adults at 65 and for athletic swimmers at 260. Using these frequencies the $E_o$ was calculated as a yearly average. Next, that $C_{water}$ was calculated at which the yearly average equalled 20% of the long term toxicological reference value or, for genotoxic carcinogens, the $C_{water}$ at which the yearly average equalled the extra cancer risk level of 1 in 100,000.

Based on the results of the calculation, for HAAs limits for swimming-pools can be derived. These are shown in the table below.

**Table 10: Haloacetic acids (HAAs) for swimming pools**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Monochloroacetic acid | 800 | Swimming-water limit derived in the present document | Based on TDI as reported by WHO, 20% of TDI allocated to swimming-water |
| Dichloroacetic acid | 1500 | Swimming-water limit derived in the present document | Compound is genotoxic carcinogen, extra cancer risk level of $1.10^{-5}$ as reference |
| Trichloroacetic acid | 8000 | Swimming-water limit derived in the present document | Based on TDI as reported by WHO, 20% of TDI allocated to swimming-water |
| Monobromoacetic acid | 800 | Read across from monochloroacetic acid | Read across from monochloroacetic acid |
| Dibromoacetic acid | 1000 | Read across from dichloroacetic acid | Read across from dichloroacetic acid |
| Tribromoacetic acid | 8000 | Read across from trichloroacetic acid | Read across from trichloroacetic acid |
| Dibromochloroacetic acid | 8000 | Read across from trichloroacetic acid | Read across from trichloroacetic acid |

**Halo-aldehydes (chloral hydrate and bromal hydrate)**

The following values are available:

**Table 11: Halo-aldehydes (chloral hydrate and bromal hydrate)**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Chloral hydrate | 100 | WHO drinking- | TDI based on liver effects, 80% of |

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| | | water guideline | TDI allocated to drinking-water, drinking-water consumption 2 L per day |
| Bromal hydrate | 100 | Read across from chloral hydrate | Read across from chloral hydrate |

Chloral hydrate has a low Henry coefficient (estimated value 0.00057 Pa.m$^3$/mol) and therefore inhalation exposure in swimming-pools is estimated to be low only. Dermal penetration is also considered limited only (Kp value of 0.0039 cm/h as measured in human skin in vitro versus 0.16—0.21 cm/h for THMs in the same test system) (Trabaris et al. 2012; Xu et al. 2002). In view of this, using drinking-water guidelines is considered adequately protective.

**Haloacetonitriles**

The following values are available:

**Table 12: Haloacetonitriles**

| Compound | Limit in [µg/L] | Origin of limit | Toxicological basis for limit (derivation) |
|---|---|---|---|
| Dichloroacetonitrile | 20 | WHO drinking-water guideline | TDI based on liver effects, 20% of TDI allocated to drinking-water, drinking-water consumption 2 L per day |
| Dibromoacetonitrile | 70 | WHO drinking-water guideline | TDI based on growth effects, 20% of TDI allocated to drinking-water |
| Bromochloroacetonitrile | 20 | Read across from dichloroacetonitrile | Read across from dichloroacetonitrile |

For the different haloacetonitriles, Trabaris et al. (2012) report Kp values for dermal penetration of 0.099-0.167 cm/h. This value was determined in human skin in vitro; in this system the Kp for THMs was between 0.16 and 0.21 cm/h. Based on this the dermal penetration of the haloacetonitriles is expected to comparable to that of the THMs. For dichloroacetonitrile and dibromoacetonitrile Henry coefficients of 0.379 and 0.041 Pa.m$^3$/mol have been reported (Jin et al. 2012) (compared to 370 Pa.m$^3$/mol for chloroform). Based on these values inhalation exposure for dihalonitriles is estimated to be low only. In view of this, using drinking-water guidelines is considered adequately protective.

# Appendix 3. Methods for chemical analysis of marker DBPs

**Table 13: Analytical methods**

| DBP | Analytical method |
|---|---|
| Trihalomethanes (expressed as chloroform) | ISO 15680:2003 |
| Bromate | ISO 15061:2001 |
| Chlorate & chlorite | ISO 10304-4:1999 |
| Haloacetic acids | USEPA Method 552.3; USEPA Method 557 |
| Chloral hydrate | USEPA Method 551.1 |
| Bromal hydrate | USEPA Method 551.1 |
| Haloacetonitriles | USEPA Method 551.1 |
| Trihaloamines | Hery et al. (1995), INRS (2015)(also VITO 2015) |

# Appendix 4. Potential relevance of PTs regarding the human health risk assessment of DBPs in the context of biocides authorisation (written commenting round).

**Table 14: Potential relevance of PTs regarding the human health risk assessment of DBPs in the context of biocides authorisation.**

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| PT 1: Human hygiene | Products in this group are biocidal products used for human hygiene purposes, applied on or in contact with human skin or scalps for the primary purpose of disinfecting the skin or scalp. | Yes | **NL**: Not expected to consist of halogenated disinfection oxidising agents.<br>(Although iodinated products may be used, the mode of action of these is different)<br>**SK**: Not relevant for halogenated actives<br>**IND:** Two uses supported: hand-wash and foot-wash. Consider hand-wash worst case for both HH. Organic molecules (e.g. fatty acids) on the skin could in principle react with chlorine in a hand-wash to produce DBP(s). Consideration of possible absorption of such DBP(s) would be needed.<br>The calculation would require selection of relevant **types** of molecules known to be in sweat/secretions on skin e.g. fatty acids. Once the latter selection has been achieved, choose the **nearest structurally representative DBP(s)** from the list referred to in the 'thought starter' **with (hopefully) a toxicity reference value available**, then calculate maximum amount (mg) of each of these 'potential' DBP(s) based on application of chlorine hand-wash (**max 0.02 w/v**) and assumption that the available chlorine has a 1:1 molar conversion for each DBP (worst-case). Base the HH assessment on initial worst-case assumption of 100% absorption of each DBP (then 75% if fails at 100%). The calculations would assume no loss through evaporation of the DBPs from the skin, i.e. worst-case. Perhaps such evaporation could be used as a refinement if really needed. |

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| | | | Consideration of possible inhalation to any volatile DBP may need to be considered. Although expected to be negligible. |
| PT 2: Disinfectants and algaecides not intended for direct application to humans or animals | Products used for the disinfection of surfaces, materials, equipment and furniture which are not used for direct contact with food or feeding stuffs. | Yes | **NL**: see argumentation PT4 (e.g. cleaning in day care centre: exposure to DBPs in air and contact with cleaned surfaces –inhalation and dermal exposure). |
| | Usage areas include, inter alia, swimming pools, aquariums, bathing and other waters; air conditioning systems; and walls and floors in private, public, and industrial areas and in other areas for professional activities. | Yes | **NL**: swimming pools already covered. Surface area less critical, but need to be addressed. Air-conditioning systems also need to be addressed.<br>**IND:** Clearly, the worst-case of exposure to DBPs is **chlorinated** swimming pools which would cover all uses in PT2. It may of course be necessary to do other specific DBP calculations in other use-patterns that the applicant is supporting, for example to cover hard surface disinfection, **but only in the event swimming pools were to fail, in order to show a safe use within PT2.**<br>[Note: calculations for hard surface disinfection would be expected to show much lower dermal exposure than for PT1 hand-wash containing the same concentration of active chlorine. Only exposure via dermal route would be expected to be relevant for DBP resulting from active chlorine reacting with human secretions (?) on surfaces.<br>Consideration of possible inhalation to any volatile DBP may need to be considered although expected to be negligible. |
| | Products used for disinfection of air, water not used for human or animal consumption, chemical | No | **NL**: use in air conditioners should be considered, other scenarios not relevant |

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| | toilets, waste water, hospital waste and soil. | | |
| | Products used as algaecides for treatment of swimming pools, aquariums and other waters and for remedial treatment of construction materials. | Yes | **NL**: already covered above |
| | Products used to be incorporated in textiles, tissues, masks, paints and other articles or materials with the purpose of producing treated articles with disinfecting properties. | No | **NL**: halogenated actives not considered suitable for these scenario's, as the quality of the products would be reduced. |
| | | | **SK**: Uses potable water already containing DBP<br>Variable exposure to DBP depending on use. No release/exposure scenario is as extensive or chronic in comparison to exposure from DBP in potable water. |
| PT 3: Veterinary hygiene | Products used for veterinary hygiene purposes such as disinfectants, disinfecting soaps, oral or corporal hygiene products or with anti-microbial function. | Yes | **NL**: this PT is considered less relevant for consumer exposure. However, the scenario for disinfection of housing may be hazardous. Even though the operator (professional) can use protective measures, a safe re-entry period must be included in the labels to ensure consumer (bystander) exposure.<br>**SK**: Uses potable water already containing DBP.<br>Spraying and fogging scenarios, incidental contact directly after application. Egg washing, footbaths. Potential for food/feed residues.<br>**IND:** Use-patterns: teat dips, footbaths, animal house disinfection. Animal houses considered worst-case.<br>Spraying of animal houses is considered to represent worst-case, in terms of potential for dermal |

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| | | | exposure due to splashing of DBPs formed when active chlorine solution contacts surfaces and potential for exposure to volatile DBP(s) in an enclosed place formed by contact with residual material left over after any water-washing.<br>**NOTE:** The ESD for PT3 does state that disinfection takes place after **'thorough cleaning'** so in actual fact, the amount of residual organic materials on walls and floors should be relatively low prior to exposure to active chlorine, and hence DBPs exposure would also be relatively low. |
| | Products used to disinfect the materials and surfaces associated with the housing or transportation of animals. | Yes | |
| PT 4: Food and feed area | Products used for the disinfection of equipment, containers, consumption utensils, surfaces or pipework associated with the production, transport, storage or consumption of food or feed (including drinking water) for humans and animals. | Yes | **NL**: DBPs can occur in foods that have come into contact with disinfected processing machines etc. or with packaging materials treated with biocides.<br>In this context the active substance should also be addressed in the context of MRL setting (methodology still in progress). If DBPs are the primary source of residues, they should be considered in MRL setting. Exposure is expected to be limited to the oral route.<br>**SK**: Primary source of DBP, potable water used for all other PT. Acts as baseline for DBP concentration. All water for human consumption treated in line with Drinking Water Directive and Regulations. Comparative standards applied across EU<br>High daily exposure through drinking and bathing. All population.<br>**IND**: Use-patterns are CIP and hard surface disinfection.<br>Hard surface disinfection probably |

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| | | | worst-case, since actual hand contact of possible DBPs formed is more likely than from CIP. Possible, but likely negligible inhalation exposure due to formation of volatile DBPs. Can be considered and dismissed with a generic air concentration calculation perhaps, to show extremely low concentrations of DBPs in air are likely from this type of use-pattern. Although potentially CIP could present an oral exposure risk, there is the intention for a **'water-rinse'** instruction after use of any active chlorine solution, before any food product is passed through treated lines. Therefore, no DBP will go into food/drink from CIP processes. So, oral exposure to DBPs should be negligible. |
| | Products used to impregnate materials which may enter into contact with food. | No | Not expected to include halogenated oxidising active substances. |
| PT 5: Drinking water | Products used for the disinfection of drinking water for both humans and animals | Yes | **NL**: Chemicals for use in drinking water is regulated on national level. In NL, biocides are allowed to be used in (contact with) drinking water, as long as the active substance is approved as a biocide (PT5, or PT4 for drinking water contact materials). No additional assessment will be performed for possible BPD's. Only for THM's (chloroform, bromoform, dibromochloromethane and bromodichloromethane) a restriction is set in the Drinking water Directive (98/83/EC).<br>Tap water is used for all kinds of other purposes (drinking, cleaning, showering).<br>**SK**: Primary source of DBP, potable water used for all other PT. Acts as baseline for DBP concentration. All water for human consumption treated in line with Drinking Water Directive and Regulations. Comparative standards applied |

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| | | | across EU<br>High daily exposure through drinking and bathing. All population.<br>**IND:** For animal health, exposure to DBPs is not relevant because there will be negligible transfer of organic matter (i.e. saliva **containing molecules that can react with active chlorine**) from the animals' mouths (or **none** in the case of chicken/turkey beaks) to the water, hence other animals drinking water in the same circulatory system on a farm, will be exposed to negligible amounts of any DBP."<br>For human and animal drinking water the organic matter present in the drinking water would be expected to be low and hence DBPs would be expected to be present at a negligible level |
| PT6: Preservatives for products during storage | Products used for the preservation of manufactured products, other than foodstuffs, feedingstuffs, cosmetics or medicinal products or medical devices by the control of microbial deterioration to ensure their shelf life.<br>Products used as preservatives for the storage or use of rodenticide, insecticide or other baits. | No | **NL**: Not expected to include halogenated oxidising active substances. |
| PT7: Film preservatives | Products used for the preservation of films or coatings by the control of microbial deterioration or algal growth in order to protect the initial properties of the surface of materials or objects such as paints, | No | **NL**: Not expected to include halogenated oxidising active substances. |

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| | plastics, sealants, wall adhesives, binders, papers, art works. | | |
| PT 8: Wood preservatives | Products used for the preservation of wood, from and including the saw-mill stage, or wood products by the control of wood-destroying or wood-disfiguring organisms, including insects. This product-type includes both preventive and curative products. | No | **NL**: Not expected to include halogenated oxidising active substances. **SK**: Uses potable water already containing DBP for treatment process. |
| PT 9: Fibre, leather, rubber and polymerised materials preservatives | Products used for the preservation of fibrous or polymerised materials, such as leather, rubber or paper or textile products by the control of microbiological deterioration. This product-type includes biocidal products which antagonise the settlement of micro-organisms on the surface of materials and therefore hamper or prevent the development of odour and/or offer other kinds of benefits. | No | **NL**: Not expected to include halogenated oxidising active substances. **SK**: Uses potable water already containing DBP for manufacturing process. DBP generation not expected from use of materials and not in high concentration (leaching) |
| PT 10: Construction material preservatives | Products used for the preservation of masonry, composite materials, or other construction materials other than wood by the control of microbiological, and algal attack. | No | **NL**: Not expected to include halogenated oxidising active substances. **SK**: Uses potable water already containing DBP for manufacturing process. DBP generation not expected from use of materials and not in high concentration (leaching) |
| PT 11: Preservatives for liquid- | Products used for the preservation of water or other liquids used in | No | **NL**: to discuss whether swimming at discharge point is hazardous or can be minimized by precautionary |

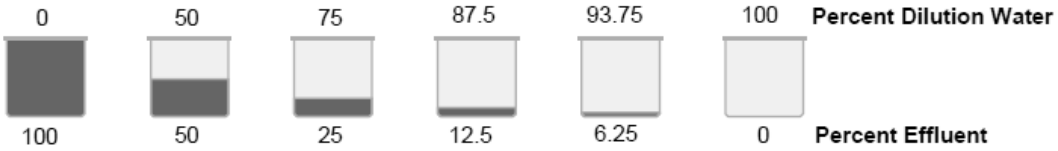
| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| cooling and processing systems | cooling and processing systems by the control of harmful organisms such as microbes, algae and mussels. Products used for the disinfection of drinking water or of water for swimming pools are not included in this product-type. | | safety measures. Otherwise not directly relevant for human exposure.<br>**SK**: Uses potable or surface water already containing DBP prior to preservative inclusion. Minimal exposure to general public from use. |
| PT 12: Slimicides | Products used for the prevention or control of slime growth on materials, equipment and structures, used in industrial processes, e.g. on wood and paper pulp, porous sand strata in oil extraction. | No | **NL**: to discuss whether a significant amount of DBPs formed during the process are still present in paper and board when used as food packaging material and/or whether migration limits should be set. It is noted that the safety of DBPs is not assessed within the framework of FCM's which are except for plastic FCM mainly regulated on national level.<br>**SK**: Uses potable water already containing DBP prior to preservative inclusion.<br>Minimal exposure to general public from use, would be exposure to residues in material made in process using water containing slimicide, e.g. paper. |
| PT 13: Working or cutting fluid preservatives | Products to control microbial deterioration in fluids used for working or cutting metal, glass or other materials. | No | **NL**: Not expected to include halogenated oxidising active substances.<br>**SK**: Uses potable water already containing DBP prior to preservative inclusion. Minimal exposure to general public from use, would be exposure to residues in material made in process using water containing preservative. |
| PT14-20 pest control | | No | **NL**: Not expected to be disinfectants and/or to include halogenated oxidising active substances. |
| PT21: antifouling | Products used to control the growth and settlement of fouling organisms (microbes and higher forms of | No | **NL**: Not expected to include halogenated oxidising active substances.<br>**SK**: DBP present in seawater. |

| PT | Description of use area and products | Relevance for HH | Argumentation |
|---|---|---|---|
| | plant or animal species) on vessels, aquaculture equipment or other structures used in water. | | |
| PT 22: Embalming and taxidermist fluids | Products used for the disinfection and preservation of human or animal corpses, or parts thereof. | No | **NL**: Not expected to include halogenated oxidising active substances.<br>**SK**: Uses potable water already containing DBP in treatment process. Exposure minimal from treated items as release to soil. |

# Appendix 5. Whole Effluent Testing

Biological testing of effluents has been applied since a long time to evaluate the efficiency of (waste) water treatment in removing pollutants, or to assess the environmental impact of discharges (Baltus et al., 1999; Hernando et al., 2005; Mendonca et al., 2009; Meric et al., 2005; Oral et al., 2007; Selcuk et al., 2007; Tisler et al., 2004; Tonkes et al., 1999; Tothill and Turner, 1996; Rizzo, 2011; FEI, 2010; Ospar, 2005). When applying whole effluent testing (WET), the usual approach is to classify effluents according to the dilution or concentration rate which is needed to reach a certain effect level in a bioassay. To this end, effluent and control water are mixed in varying proportions to create a dilution series (see Figure 2; copied from US-EPA, 2010). The dilution series is then used in aquatic toxicity tests, similar to a concentration range, and the endpoint of the test (e.g. L/$EC_x$, NOEC) is expressed as a dilution percentage instead of a concentration.

**Figure 5: Principle of WET**




As for the "normal" ecotoxicity endpoints, it has to be decided which dilution is acceptable. Baltus et al, (1999), used the following classification scheme:

**Table 15: Classification scheme**

| Lowest toxicity result | Classification |
|---|---|
| < 1 % v/v (dilution ≥ 1:100) | very strongly acutely toxic |
| 1-10 % v/v (dilution 1:10-1:100) | strongly acutely toxic |
| 10-50 % v/v (dilution 1:2-1:10) | moderately acutely toxic |
| 50-100 % v/v (dilution 1:2-undiluted) | little acutely toxic |
| > 100 % v/v (concentrated[10]) | not acutely toxic |

Later on, the effect classes 10-50 % v/v and 50-100 % v/v were combined into one effect class 10-100% v/v, and the class names were slightly changed (Tonkes et al., 1999).

Instead of a dilution percentage, the effects may also be expressed as Toxic Units (Baltus et al., 1999; US-EPA, 2010). If in an acute test the LC50 is 60% effluent, the result is equivalent to 100/60 = 1.7 acute Toxic Units ($TU_a$). Similarly, if the NOEC from a chronic test is 40% effluent, the result is equivalent to 100/40 = 2.5 $TU_c$. The results of the test are then compared to water quality criteria expressed as TU, considering upstream, downstream and discharge flow rates (see US-EPA, 2010 for more details).

[10] In the original paper, the >100% class is indicated as undiluted ('onverdund' in Dutch), but concentrated would be more appropriate.

Germany, Turkey and Slovenia have implemented discharge limits based on this principle. In Turkey, the effluent should not cause >50% mortality to fish when diluted for at most 3 to 4 times (Selcuk et al., 2006). In Slovenia, effluent discharge is not permitted if the effluent has to be diluted more than four times to prevent 50% immobility of *Daphnia magna* in a 24-hours test (Tisler et al., 2004). In Germany WET is current practice for regulation of discharges. In the wastewater ordinance[11] acceptable effluent dilutions are listed for several tests (toxicity to fish eggs, *Daphnia*, algae and luminescent bacteria) depending on industry sector. A number of these criteria are relevant in terms of biocide emissions.

Another assessment scheme has been proposed in a Dutch research project (Maas et al., 2003). Although never implemented in environmental policy, it may be worthwhile to present it here as an example: the effect of an untreated sample on aquatic organisms (e.g. daphnids, algae, bacteria, fish) is determined in acute or chronic tests, and the effect of the sample is acceptable if in three acute tests there is no effect in a 10-times concentrated sample (concentration is performed with XAD-columns), and in three chronic tests there is no effect of the untreated sample. If on the basis of this preliminary assessment a risk is identified, a refined risk assessment is proposed in which on the basis of at least four chronic results the concentration factor is calculated at which potentially 5% of the species is affected (analogous to the SSD-approach).

A comprehensive overview of the use of bioassays by jurisdictions in North America, the European Union, and Asia/Pacific up to 2004 is presented in Power and Boumphrey (2004). From this paper it appears that WET for permits is mainly used in North America (USA and Canada), but according to the US-EPA manual for permit writers (US-EPA, 2010), WET is used as a second approach, in addition to a chemical-specific approach. Most European countries focus on BAT and limit values for individual chemicals. With the exception of Germany and Sweden, WET is not applied on a routine regulatory basis, although in a number of countries it may be occasionally used for licensing (Power and Boumphrey 2004). In Sweden, WET is applied for monitoring purposes by the SE-EPA (Bengtsson et al., 2009; Naturvårdsverket,. 2011) as well as in the development of a monitoring program for the assessment of sewage effluent (Lilja et al., 2010). WET is also discussed as a tool for the assessment of hazardous substances in the Baltic Sea region. OSPAR considers WET as a complementary tool to a substance-based approach (OSPAR, 2005).

[11] Federal Ministry for the Environment Nature Conservation and Nuclear Safety Germany. 2004. Promulgation of the New Version of the Ordinance on Requirements for the Discharge of Waste Water into Waters (Waste Water Ordinance - AbwV) of 17. June 2004. Bonn, Germany.

# Appendix 6. Summary of information from the EU-RAR on NaOCl

This Appendix summarises information from the EU-RAR on sodium hypochlorite (EC,2007). Note that this is not a worked-out case study following the risk assessment strategy developed in this guidance, but an illustration of a previous risk assessment. Information from this assessment and the strategy followed may also be useful for biocides authorisation dossiers. For those use scenarios that may be relevant for biocides assessment, Table 16 (see next page) summarises the key-parameters listed in section 3.3.2. The EU-RAR risk assessments for uses related to PT2, PT11 and PT12 are discussed in more detail in the following sections. Information from other literature sources is added where relevant.

## A6.1 Summary of use scenarios from the EU-RAR

**Table 16: Summary of use scenarios from the EU-RAR with potential relevance for biocides authorisation.**

| Use Scenario | Key Parameters | | | | | | | DBP Formation | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | pH | Substrates present | Cl:C | 'Free' halogen residual | Applied Dose / Concn | Contact Time | Temp | AOX Conversion | THM yield / concn | HAA yield / concn |
| **Household Cleaning** | | Proteins, carbohydrates, fats (PC&F), minor contaminants | | | | | | | | |
| • Laundry | 8 - 11 | PC&F, minor contaminants | <1 | No | 200 mg/L NaOCl | 15 min | 38 – 50 deg C | 2.6% | 10% AOX | 11.4% AOX |
| • Hard Surface and toilet | 8 - 11 | PC&F, minor contaminants | High | Yes in toilet | | < 5 minutes – 8 hrs | Ambient | 0.1% (limited by substrates) | 12% AOX | 15% AOX (10% TCA) |
| • Drain | 7 - 9 | PC&F, minor contaminants, ammonia / amino-nitrogen | Low <<1 | No | | 1 hr modelled | Ambient | 1.5% | 8.8% AOX | 5% AOX |
| **Pools** | 6.5 – 8.5 | PC&F, minor contaminants | | Up to 1.25 mg/L free chlorine residual | <5mg/L | Continuous | Up to 30 deg C | 0.8%, 700 µg/L | 170 µg/L | 502 µg/L |
| **Sewage Disinfection** | 6.6 - 8 | PC&F, multiple contaminants, ammonia / amino-nitrogen | Low | Residual 2 mg/L as CAC during contact time | 40 mg/L | 1 hr | Ambient | 2% | 70 µg/L | 35 µg/L |
| **Potable Water** | 6 – 8 | Natural organic matter (NOM) esp. humic, fulvic substances and PC&F | | | | | | 1 – 5% | | |
| • Groundwater | 6 – 8 | Limited NOM | 1 – 1.5 | Initial, Residual <0.5 mg/L | <<5mg/L | <1 hr, then residual | Ambient | | 5 µg/L | 2 µg/L |
| • Surface water DWD compliant | 6 – 8 | NOM, PC&F and other aquatic contaminants | <1 | Initial, Residual <0.5 mg/L | <5mg/L | <1 hr, then residual | Ambient | | 70 µg/L | 24.5 µg/L |

| Use Scenario | Key Parameters | | | | | | | DBP Formation | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | pH | Substrates present | Cl:C | 'Free' halogen residual | Applied Dose / Concn | Contact Time | Temp | AOX Conversion | THM yield / concn | HAA yield / concn |
| | | | | | | | | | | |
| • Upland acid | 6 - 7 | High NOM | <1 | Initial, Residual <0.5 mg/L | <5mg/L | <1 hr, then residual | Ambient | | | 255 µg/L |
| **Cooling Water** | 6.5 - 8 | As potable water but including seawater and contaminants | | 0.5 mg/L TRO at condensers | <5mg/L | <10 mins, then residual | Ambient | <1% | 30 µg/L | 10 µg/L |

## A6.2 Sewage treatment (PT2)

### A6.2.1 Occurrence of DBPs

In the EU-RAR (EC, 2007), sewage treatment was considered as a realistic worst case for the use of sodium hypochlorite in PT2. The range of chlorinated by-products that may be formed during sewage chlorination is potentially wide since substantial quantities of many different substrates are present (DeBorde and Von Gunten, 2008; Jolley et al., 1982; Pickup, 2010; Sun et al., 2009ab). In a study to examine the effect of different disinfection treatments on the presence of micro-pollutants, more than 100 different compounds were identified, and it was concluded that chlorination removed some mutagenic micro-pollutants, but produced others (Jolley et al., 1982). According to the EU-RAR (EC, 2007), there have been relatively few attempts to identify and quantify these in relation to typical operating conditions. According to the Euro Chlor document (Pickup, 2010), trihalomethanes (THMs) and halogenated acetic acids (HAAs) predominate. Overall incorporation rates of applied available chlorine into chlorinated by-products, measured as adsorbable organic halogens (AOX) or dissolved organic halogen (DOX) are of the order of 0.5 – 2% depending for example on contact time and Cl:DOC ratio. In simulation studies, it was shown that formation of THMs and HAAs increases exponentially with chlorine dose, while variations in contact time, pH and temperature resulted in different patterns of formation of these two groups (Sun et al., 2009ab). The EU-RAR refers to a study performed by WRc in 1993 for the UK National Rivers Authority (Davis et al., 1993) on an operating sewage disinfection plant. This study is also used to calculate formation of DBPs in the sewer resulting from household use of chlorine, and a description can be found in that particular section of the EU-RAR (p. 51-52), which is copied here:

> "Chlorine residuals maintained around 55 – 58 mg/L, average chloroform levels rose from 4 µg/L in the unchlorinated effluent to 71 µg/L following chlorination i.e. an increase of 67 µg/L (equivalent to 60 µg/L AOX). Other THM levels rose from 0.8 to 3.3 µg/L = 2.5 µg/L (equivalent to approx 2.4 µg/L AOX). The total AOX levels rose from an average of 91 µg/L in unchlorinated effluent to 801 µg/L following chlorination, an increase of 710 µg/L. In laboratory experiments using 40 mg/L chlorine for 1 hour, carried out during the same series of studies, estimates of trichloracetic acid formation (detected by GCMS as methyl ester) were 17 µg/L (equivalent to 10 µg/L AOX) and dichloracetic acid 19 µg/L (equivalent to 10 µg/L AOX) whilst the average AOX level rose from 188 µg/L to 625 µg/L, an increase of 437 µg/L. On the basis of ratios seen in other scenarios other HAA concentrations are likely to be around 10% of the combined TCA + DCA concentration i.e. another 2 µg/L AOX. The above data can be used to estimate the fraction of formed AOX that will be trihalomethanes (8.8%), TCA (2.3 %) and other HAAs including DCA (2.7%) in the domestic sewer reaction scenario."

Small quantities of chlorinated phenols have been seen to be formed in sewage chlorination experiments, of the order of 0.01% of the available chlorine dose. The phenols formed were predominantly 2-chloro- and 2,4-dichlorophenols with some formation of 2,4,6-trichlorophenol only at high (100 mg/L) applied doses (Davis et al., 1993, cited in EC, 2007; Pickup, 2010. These studies showed no increase in pentachlorophenol levels following chlorination, and possibly a decrease at lower doses (20 and 40 mg $Cl_2$/L).

### A6.2.2 Risk assessment in the EU-RAR

The risk assessment in the EU-RAR is carried out considering continuous discharge of 70 µg/L for THMs, and 35 µg/L for HAAs. The latter value probably originates from the combined tri- and dichloroacetic acid fraction (17 and 19 µg/L). Expressed as AOX, the estimated discharge is 800 µg/L, based on a formation rate of DBPs of 2% of the higher chlorine dose (40 mg $Cl_2$/L). A 10-fold dilution factor is used. The PNEC for chloroform is

considered to be representative for all THMs, since the ecotoxicity for the other THMs is equal to or less than that of chloroform. Although the PNECs for monochloroacetic acid (MCA) and dichloroacetic acid (DCA) are potentially lower than that for trichloroacetic acid (TCA), MCA and DCA are less stable and calculated PECs in the EU-RAR are negligible. Therefore, a risk assessment based on a PEC/PNEC-comparison for TCA is considered to be a conservative estimate for all HAAs[12]. A potential risk was identified for HAAs, but the risks were considered acceptable in view of a refined assessment (see below). Halogenated macromolecules, such as chlorinated proteins are considered as a major by-product (5-50%). Halogenated aldehydes, ketones, acetonitriles and aminoacids are identified as minor by-products (0.5-5%), halogenated phenols as a trace compound (<0.5%). These groups are not further assessed, but are also assumed to be covered by the refined risk assessment.

### A6.2.3 Refined risk assessment

A simulation study was used in the EU-RAR to address the potential effects of DBPs resulting from sewage chlorination (for details, see (EC, 2007), p. 99-101, and Annex 7). Untreated and treated samples of raw settled sewage (RSS) were prepared. RSS was sampled, part was chlorinated and subsequently dechlorinated (i.e. residual chlorine was removed), the other part was left untreated. These samples were then compared to assess whether chlorinated DBPs formed in the chlorination process were toxic, or potentially bioaccumulative and persistent. Toxicity endpoints for bacteria (bioluminescence of *Vibrio fischerii*), algae (growth rate of *Pseudokirchneriella subcapitata*) and crustacea (survival and reproduction of *Daphnia magna*) were expressed as dilution percentages. Biodegradation was determined in a Zahn-Wellens test and bioaccumulation was tested by exposing SPME fibres to samples of untreated and treated RSS before and after degradation in a Zahn-Wellens test. The quantities of chlorinated organics collected on the fibres were measured using two different methods: a total organo-halide (TOX) technique and by measuring the area under the curve produced by injection into a GC-MS operating in ECD mode. Chlorination of raw sewage was chosen to be the test conducted because it was considered to represent a “worst case” that would cover several other use scenarios where the substrates (i.e. natural organic matter including proteins, carbohydrates and fats) and reaction conditions (i.e. pH > 6 with excess available chlorine) were similar or less severe, e.g.:

- Wastes from household bleach use discharged to an STP
- Wastes from industrial and institutional cleaning discharged to an STP;
- Water from swimming pools discharged to an STP;
- Wastes from drinking water treatment facilities discharged to an STP;
- Treated cooling waters discharged directly to a receiving water;
- Treated swimming pool water discharged directly to a receiving water;
- Sewage disinfected prior to discharge to a receiving water.

If no unacceptable effects are observed upon chlorination of raw sewage, this is considered applicable to the other uses as well. In this way, exploring one worst case scenario in a refined risk assessment is cost efficient as compared to testing all scenarios separately.

The conclusions of the experiment were as follows (copied from EU-RAR):

[12] Note that new data have been generated for TCA after completion of the EU-RAR.

- For all the taxa tested, the mixture of by-products formed by chlorination of raw settled sewage did not increase toxicity relative to that measured in the untreated raw settled sewage.
- Chlorination of the raw settled sewage did not reduce its biodegradability and showed no evidence of production of additional non-degradable substances to those present in raw settled sewage.
- Chlorination of the raw settled sewage did increase the amounts of lipophilic chlorinated substances capable of being absorbed by SPME fibres (solid phase micro extraction) prior to biodegradation. However, there was no increased absorption after biodegradation indicating that any potentially bioaccumulative chlorinated substances formed were biodegradable.

On the basis of this study, it was concluded that no unacceptable risks were to be expected, despite the fact that for some groups of compounds PEC/PNEC >1 were obtained in the first instance.

## A6.3 Cooling water systems (PT11)

### A6.3.1 Occurrence of DBPs

According to the EU-RAR (EC, 2007), "the halogenated organic by-products formed during cooling water chlorination will broadly parallel those forming in drinking water chlorination. The principal families detected are thus the THMs, which are normally the most prevalent, followed by HAAs and haloacetonitriles. Small quantities of halophenols are sometimes detected." Three monitoring studies are presented in the EU-RAR (Berbee, 1997; Jenner et al., 1997; Khalanski, 2002), the information of which is summarised below.

The first study cited in the EU-RAR presents monitoring for 10 coastal power plants in the UK, France and the Netherlands, applying chlorination for disinfection (Jenner et al., 1997). Concentrations were measured in the undiluted effluent stream of power plants that applied chlorine dosages between 0.5 and 1.5 mg $Cl_2$/L. According to this study, bromoform was the most abundantly present DBP, and dibromoacetonitrile (DBAN) the second highest in concentration. Table 17 below presents a summary of these monitoring data, based on the original publication.

**Table 17: Measurement of by-products of hypochlorite application in cooling water of coastal power stations, summarising data from Jenner et al. 1997**

| Compound | # samples | Range of average values per sampling [µg/L] | Overall average [µg/L] |
|---|---|---|---|
| Bromoform | 90 (10 stations) | 0.72-29.2 | 16.32 ± 2.10 |
| DBAN | 29 (8 stations) | <0.1-3.15 (max. 6.5) | 1.48 ± 0.56 |
| BDCM + DBCM | 3 stations | 0.6 – 0.8 | |
| Chloroform | 10 stations | <0.1 (single point 1.5) | |
| 2,4,6-tribromophenol | 3 stations | 0.12-0.29 | |
| 2,4-dibromophenol | | max. 0.055 | |

DBAN = dibromoacetonitrile
BDCM = bromodichloromethane
DBCM = dibromochloromethane

Jenner et al, (1997) also carried out sampling along the plume of two coastal power stations in the UK. A gradual decrease in bromoform concentrations concurrent with a

decline in water temperature was observed. At the first location, bromoform concentrations declined from 9.85 µg/L at 375 m from the outfall to 0.18 µg/L at about 5 km distance. Dibromoacetonitrile (DBAN) was not detected, except for one sampling at 2 km distance (0.21 µg/L). At the second location, 13.5 to 14 µg/L was measured at the outfall, declining to 1.0 µg/L at 1.3 km distance. DBAN declined from 1.8 µg/L at the outfall to <0.1 µg/L at 1.3 km distance.

The second study referred to in the EU-RAR is from Berbee (1997), who summarised information on THM formation based on American research (Table 18). From these data, Berbee estimates that about 1% of the dosed chlorine is present as THMs (haloforms), and points at the fact that brominated DBPs will be formed in the presence of bromide, which is present at relatively high levels in seawater. This was also recognised by other authors (DeBorde and Van Gunten, 2010; Pickup, 2010).

**Table 18: Formation of THMs upon chlorine treatment of cooling water at different sites. Table from Berbee (1997)**

| Surface Water | Bromide content [µg/L] | Dose [mg $Cl_2$/L] | Haloform formation [%] | $CHCl_3$ [µg/L] | $\Sigma CHBr_xCl$ [µg/L] |
|---|---|---|---|---|---|
| **Freshwater** | | | | | |
| Columbia river | 4 | 2.9 | 0.80 | 12.7 | - |
| Ohio river | ? | 4.6 | 0.36 | 6.5 | 4.1 |
| Lake Michigan | ? | 3.4 | 0.21 | 2.3 | 2.4 |
| Missouri river | 75 | 4.2 | 0.94 | 11.5 | 16.1 |
| Tennessee river | ? | 4.5 | 1.12 | 22.9 | 7.8 |
| Lake Norman | ? | 4.1 | 0.21 | 3.6 | 1.7 |
| Connecticut river | ? | 4.6 | 0.91 | 21.6 | 2.9 |
| **Saltwater** | | | | | |
| Cape Fear | 65000 (est.) | 5.2 | 1.2 | - | 73 |
| San Onofre | 65000 (est.) | 3.1 | 0.41 | - | 15 |

In the same report Berbee (1997), a summary is presented for monitoring data on chloroform, bromoform, extractable organic halogens (EOX) and AOX in cooling water of several industrial sites in the Netherlands. Table 19 below is a translation of the original table in the report, which is not included in the EU-RAR. The data from Table 18 and 19 show that chlorination and bromination result in a similar range of compounds, but brominated instead of chlorinated compounds will dominate when bromine is used (e.g. Chemical ind. B). Brominated compounds will be dominant in water with high levels of bromide, which is particularly relevant for seawater (see power plants and Chemical ind. A in Table 19).

**Table 19: Bromoform, chloroform, EOX and AOX in cooling water from different (industrial) locations. Translated copy from Berbee (1997)**

| Location | Dose [mg $Cl_2$/L] | Concentrations in cooling water [µg/L] | | | | | Remarks |
|---|---|---|---|---|---|---|---|
| | | $CHBr_3$ | $CHCl_3$ | EOX | AOX | $BrO_3^-$ | |
| Power plants 1993-1994 | 0.8-1.5 | 16 | <1 | n.d. | n.d. | n.d. | once-through, saltwater |
| Chemical ind. A | 2.1<br>8 | 84 | n.d. | 12 | n.d. | n.d. | once-through, saltwater, shock dosing |
| Chemical ind. B | 6 | 1-8 | n.d. | 1 | 70-200 | <10 | recirculating, NaBr/HOCl, cont. dosing |
| Chemical ind. C | ? | 0.1-7 | <1 | n.d. | 200 | <2 | BCDMH; shock dosing |

n.d. = not determined
$CHBr_3$ = bromoform
$CHCl_3$ = chloroform
$BrO_3^-$ = bromate

The third study cited in the EU-RAR is a study by Electricité de France (EDF)on organic by-products from cooling water chlorination from EDF marine power stations. Measurements of the main THM and HAA formed (bromoform and dibromoacetic acid, DBAA) in cooling water samples from three power station showed bromoform levels up to 26.8 µg/L and DBAA levels up to 10.19 µg/L (Khalanski, 2002).

### A6.3.2 Risk assessment

In the EU-RAR, (EC, 2007) the risk assessment for cooling water disinfection is then performed considering continuous discharge of 30 µg/L for THMs, and 10 µg/L for HAAs, based on the monitoring data from the third study. Dilution factors of 100 and 10 were applied for emissions to sea water and freshwater, respectively. The PEC/PNEC ratios for these two groups do not point at unacceptable risks for saltwater, but are higher than 1 for freshwater. It is assumed, however, that discharge of plants operating at freshwater sites will be smaller and that continuous dosing is not likely. This assumption is not further substantiated with data, and considering the proposed uses for NaBr / HOBr it does not seem to be correct. Reference is also made to the refined assessment for sewage treatment (see Appendix 6, A6 2.3). Halogenated acetonitriles are identified as a minor by-product (0.5-5% formation), and halogenated phenols as a trace compound (<0.5% formation), and these compounds are not further assessed.

In view of the data from Berbee (1997), using data from coastal plants seems to cover the expected levels for freshwater plants, but 30 µg/L for THMs is probably not a worst case estimate for plants operating with saltwater, since bromoform levels up to 84 µg/L were measured (see Table 18). It should also be noted that bromate was not included in the risk assessment, while this compound is of interest especially for coastal plants. IMO has set a PNEC for saltwater of 140 µg/L (pers. comm. Jan Linders, GESAMP-BWWG). Although according to section 3.3.5.1, this value cannot be taken over without further evaluation, it can serve as an indication of the order of magnitude to be expected. Considering that a freshwater PNEC will most likely be higher, no unacceptable risks are to be expected for freshwater, since concentrations of bromate are reported to be <10 µg/L Berbee (1997). However, bromate data for coastal plants are not available, and a definitive conclusion on the risks for the marine environment cannot be drawn.

## A6.4 Pulp and paper (PT12)

### A6.4.1 Occurrence of DBPs

According to the EU-RAR, sodium hypochlorite as well as chlorine have been used in large amounts in the pulp and paper industry in Europe as a bleaching agent In the past. Currently this is no longer the case, mainly because the specific conditions of use i.e. the wood pulp as a broad range of organic precursors rich in phenolic molecules, long contact times with the oxidising agent and low pH conditions, were favouring the formation of chlorinated aromatic by-products and even dioxins were formed (EC, 2007). The remaining use of chlorine in the paper industry is now restricted to the use as slimicide to discourage the proliferation of unwanted micro-organisms, and as a means of breaking down the wet strength resins used in some grades of tissue when reject tissue is being processed for use in tissue manufacture. The former use is considered in PT12, while in the EU-RAR most attention is paid to the latter. Details on potential by-products arising from current pulp and paper processes due to the application of hypochlorite were not submitted by industry in the context of the EU-RAR. As for sewage treatment, it is noted in the EU-RAR that the range of DBPs formed from this use of hypochlorite can, in theory, be extremely large because of the variety of organic compounds present during use and in the sewer. THMs, HAAs, and halogenated acetonitriles, ketones and aldehydes are mentioned as the main groups of interest.

### A6.4.2 Risk assessment

In the EU-RAR, it is assumed that the risks of DBPs resulting from the use as disinfectant in pulp and paper are covered by the risk assessment for industrial use. For this latter use type, the information from household use is used, assuming that the sewer system represents a worst case with respect to the complexity of the matrix in terms of organic matter and precursors of DBPs. This assumption is not further substantiated with data, since for pulp and paper no information on DBPs was submitted in the context of the EU-RAR. For household use, a risk assessment is performed for THMs, TCA, and other HAAs. PECs for these fractions are calculated based on the above mentioned study of Davis et al, (1993. Starting from the total AOX formation resulting from household bleach, the formation of THMs, TCA and other HAAs resulting from laundry use, other use and formation in sewers is expressed as a percentage of the total AOX formation. In this way, PECs of 0.022 and 0.055 µg/L are derived for THMs and HAAs, respectively. Based on sales figures, the total chlorine use for industrial applications is assumed to be 19% of the total household use, and a dilution factor of 10 is used to estimate PECs. Resulting corrected PECs are 0.004 µg/L for THMs and 0.010 µg/L for HAAs. A potential risk was identified for HAAs in the EU-RAR mainly because of the use of chlorine for breaking down the pulp fibres, but the risks were considered acceptable in view of a refined assessment which is summarised above in Appendix 6, A6 2.3.

EUROPEAN CHEMICALS AGENCY
ANNANKATU 18, P.O. BOX 400,
FI-00121 HELSINKI, FINLAND
ECHA.EUROPA.EU