GUIDANCE

Guidance on the Biocidal Products Regulation

Volume V, Guidance on Disinfection By-Products

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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 active substance approval for Annex I inclusion (of the then BPD 98/8/EC, now Annex I inclusion for Biocidal Products Regulation (BPR)) instead of postponing it to the national authorisation stage.

From 2011 onwards NL 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 expsosure. 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 among member states, 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 further information required for the assessment. On special request of 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 sodiumhypochlorite 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 presented a combined document including both the human and environmental risk assessment in order to

[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.

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, NL organised a workshop, which was held on the 25th of June 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 of DBPs. The guidance with respect to environmental risk assessment is presented in a separate document. With this document the responsible parties for risk assessment of halogenated disinfectants can start the work on the evaluation of DBPs.

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Comment [SJ1]: CONSULTATION NOTE: The ToC shows the complete document (Part 1 and Part 2).

This will be updated at the end of the consultation procedure when the two Part s are put back together for publication.

Figures

Comment [SJ2]: **CONSULTATION NOTE:** The list of **Figures** and **Tables** shows all the figures and tables in Part 1 and Part 2. These are are numbered consecutively according to ECHA style/format.

Tables

List of Abbreviations

Comment [SJ3]: **CONSULTATION NOTE:** ECHA Secretariat to complete during PEG consultation

Standard term / Abbreviation	Explanation

1. Part 1 Human health risk assessment of disinfection by-products (DBPs)

Comment [SJ4]: **CONSULTATION NOTE:** Part 1 removed for the consultation on Part 2.

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

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

Appendix 3. Methods for chemical analysis of marker DBPs

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

2. Part 2 Environmental risk assessment of disinfection by-products (DBPs)

2.1 Introduction

2.1.1 Regulatory context

The disinfection of water with active halogen-containing biocides leads to the formation of by-products (DBPs). According to the Biocides Product Regulation (BPR [2]), the effect of residues should be evaluated in the risk assessment (see e.g. Art. 9, 1b(iii)). According to the definition in Art. 3, 1h, 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.

2.1.2 A complex issue

The main problem is that the number of potential DBPs is very high. In drinking water, more than 600 DBPs have been identified, while more than 50% of the Total Organic Halogen (TOX) formed during disinfection remains unidentified [3,4]. In a study into DBPs in indoor swimming pools in Spain in which chlorination or bromination was used for disinfection, >100 different DBPs were identified [5]. The type and amount of DBP formed depends on amongst others the availability of (organic) matter and the presence of (in)organic nitrogen compounds [6]. The operating conditions, such as concentration of the active substance, contact time, characteristics of the receiving water (pH, DOC) and environmental circumstances such as temperature and radiation are all of potential influence [6,7]. It is thus very hard to predict beforehand which compounds will be formed in a specific situation, and at which concentrations, although attempts are made to develop models for that purpose [8]. This makes a straightforward quantitative risk assessment based on PEC/PNEC comparisons for individual compounds 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.

2.1.3 Scope of the document

This document summarises background information and provides a strategy for the environmental risk assessment of DBPs. It does not contain step-by-step instructions on how to perform the risk assessment, but defines the framework for applicants to build a dossier to demonstrate a safe use of the biocide under consideration. 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, 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. These PTs are 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.

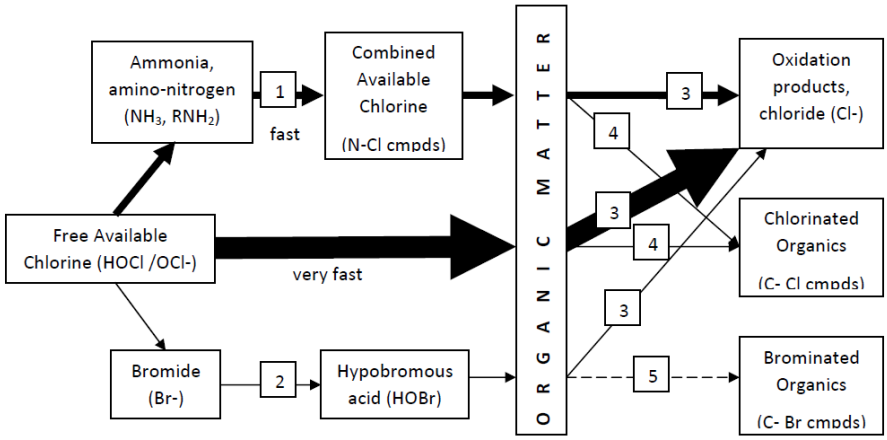
The strategy for the evaluation of DBPs that is proposed in this document is scientifically based. The implementation in the process of active substance and/or products authorisation is outside the scope of this document. In case of procedural and/or legal issues it is recommended that applicants consult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

2.2 General information on DBPs

2.2.1 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 **Error! Reference source not found.**, copied from a publication by Euro Chlor [6].

Figure 1: Schematic overview of the reactions of free available chlorine with organic matter, copied from [6]. 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 the author of the report [6] 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].'

2.2.2 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 [1,5,6,9]). 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 [10], but no iodinated DBPs were detected in bromine or chlorine-treated swimming pools in Spain [5]. The use scenario assessments in the EU-RAR [1] 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 2.3.1.3.
- 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 2.3.3.1).
- 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.

2.2.2.1 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 [6,9]. 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 [6]. Trihalomethanes are regulated under EU drinking water legislation [11], the drinking water standard for total THMs is 100 µg/L, but Member States may have set limits on a national level.

2.2.2.2 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 [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 [6]). The haloacetic acids are to varying degrees biodegradable, the most recalcitrant being TCA.

2.2.2.3 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 [5,10]. Laboratory data show halogenated aldehydes can be produced by chlorinating humic and fulvic acids (citation in [6]). 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 [6].

2.2.2.4 Halogenated acetonitriles

The four haloacetonitriles most commonly reported as by-products of active chlorine use are dichloroacetonitrile, trichloroacetonitrile, chlorobromoacetonitrile and dibromoacetonitrile [6]. 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 [12]. 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 [6]. 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 [6]).

2.2.2.5 Halogenated amides

This group, which consists of chlor- and bromacetamides, have been detected in drinking water and swimming pools [5,6,12]. As for halogenated acetonitriles, the use of chloramines is indicated as a potential cause of formation, either direct or via hydrolysis of the acetonitriles [12].

2.2.2.6 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 [6]. They have been detected in drinking water and swimming pools [5,6]. According to studies cited in [6], haloketones are relatively volatile and are susceptible to hydrolysis.

2.2.2.7 Halogenated phenols

As for the ketones, chloro- and bromophenols may be formed by reactions with humic or fulvic acid [6]. After initial addition leading to monochloro- or bromophenol, further addition leads to di- or tri- halogenated phenols. In the Euro Chlor report [6], it is suggested that formation of the tetra- or penta-forms is probably not likely, they have not been identified in swimming water [5]. Chlorinated phenols are moderately to highly lipophilic, volatility is relatively low.

2.2.2.8 Bromate

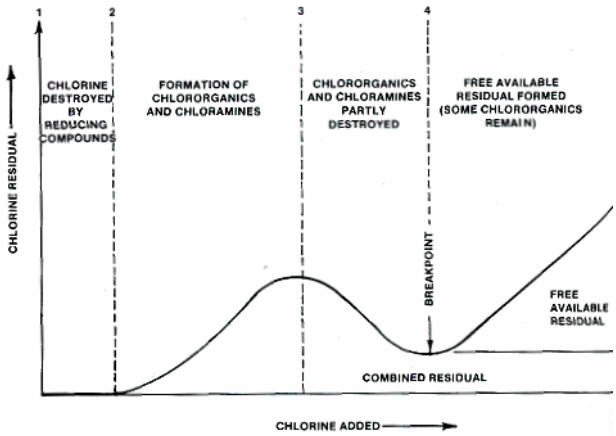
Bromate can be formed when high levels of free available chlorine are present in combination with a high pH, and when bromide is present [9]. It should also be noted that bromate may be present in sodium hypochlorite, the EU-RAR [1] mentions a range of 3-45 mg/kg as sodium bromate (ca. 2.5-38 mg/kg as 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 [9]. Bromate is regulated under EU drinking water legislation [11], the drinking water standard is 10 µg/L.

2.2.2.9 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 [6].] 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 [1]. 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 [9]. 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 [13].

Figure 2: Breakpoint curve showing the processes that occur when water is chlorinated (copied from http://water.me.vccs.edu/concepts/chlorchemistry.html)



2.3 Environmental risk assessment of DBPs

2.3.1 General principles

2.3.1.1 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 3.3.1 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.

2.3.1.2 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.

2.3.1.3 Addressing the unknown DBPs

As indicated before (see sections 2.1.2 and 2.2.2) 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 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 [14], 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 [14]. 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 1), 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 2.3.5.3) 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.

2.3.1.4 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.

2.3.2 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 2.3.5). 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.

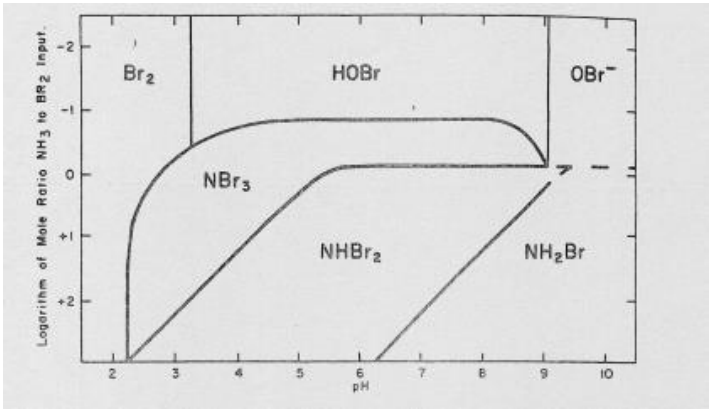
2.3.2.1 Influence of pH

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.

2.3.2.2 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 [15]. 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 [16]. As an illustration, **Error! Reference source not found.** shows the formation of different forms of brominated compounds as a function of pH and ammonia.

Figure 3: Different forms of bromine at various pH values and various concentrations of ammonia (figure copied from http://www.lenntech.com/)



2.3.2.3 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 it 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).

2.3.2.4 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.

2.3.3 Known DBPs to be included in the assessment

2.3.3.1 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 **Error! Reference source not found.**, together with representative compounds within each group. The selection is based on expert information on the principal groups of DBPs (see also 2.2.2). As stated in the previous section, it is not the intention to extend **Error! Reference source not found.** to 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 **Error! Reference source not found.**. Such information may become available in the exposure assessment, e.g. from monitoring data or based on theoretical predictions (see also section 2.3.4).

Table 1: 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) tribromomethane (bromoform) dichlorobromomethane dibromochloromethane
Halogenated acetic acids (HAAs)	monochloroacetic acid (MCA) dichloroacetic acid (DCA) trichloroacetic acid (TCA) monobromoacetic acid (MBA) dibromoacetic acid (DBA) tribromoacetic acid (TBA) bromodichloroacetic acid dibromochloroacetic acid bromochloroacetic acid
Halogenated acetonitriles (HANs)	dichloroacetonitrile trichloroacetonitrile chlorobromoacetonitrile 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 2.3.5.2). Specific compounds may be excluded based on argumentation (e.g. if they 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 2.2.2.9 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.

2.3.4 Exposure assessment

2.3.4.1 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 2.3.3 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.

2.3.4.2 Exposure assessment strategies

As indicated in section 2.3.1, 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 2.3.2 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 [9,17,18] and summarised in the EU-RAR on sodium hypochlorite [1], 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 [19-21]. 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 modeling. 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 2.3.2 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.

2.3.5 Effects assessment

2.3.5.1 Derivation of PNECs

PNECs should be derived for the relevant known DBPs (see section 2.3.3.1). 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 2.3.3.1, **Error! Reference source not found.**) 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 2.3.3.1, it may be possible that a particular biocidal use leads to formation of DBPs that are not yet addressed in **Error! Reference source not found.**. 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.

2.3.5.2 Group ecotoxicity assessment

In some cases a group assessment may be appropriate. In the EU-RAR on sodiumhypochlorite, the PNEC for chloroform was used to assess the risks of the group of THMs [1], 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.

2.3.5.3 Whole Effluent Testing (WET)

According to the procedure presented in section 2.3.1.3, 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 [22]. Furthermore, when using WET for actual effluents, the potential effects of the active substance itself 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, section 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 Annex 1 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 section A6 1.2).

2.3.6 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.

2.3.7 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 2.3.4.1).

Table 2: 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 is not likely to be performed with halogenated oxidants, but chlorination is widely used for 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 scenario's, 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. 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. 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.P roducts 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.

2.4 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 the biocidal active substance;
- a chemical assesment 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 preparePNEC-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.

2.5 References

NOTE to the reader:

Reference list includes references used in the Appendices 1-4

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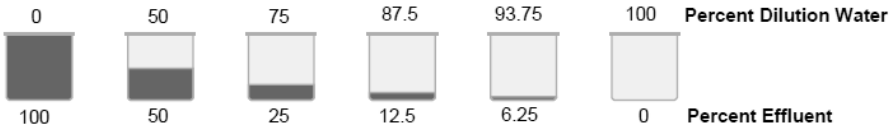
Appendix 5. Whole Effluent Testing

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 [22-33]. 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 [34]). 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 4: Principle of WET-testing



As for the "normal" ecotoxicity endpoints, it has to be decided which dilution is acceptable. Baltus et al. [22] used the following classification scheme:

Table 3: 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[2])	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 [29].

Instead of a dilution percentage, the effects may also be expressed as Toxic Units [22,34]. 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 [34] for more details).

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 [35]. In Slovenia, effluent discharge is not permitted if the effluent has to be diluted more than four times to prevent 50% immobility of *Daphnia*

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

magna in a 24-hours test [28]. In Germany WET is current practice for regulation of discharges. In the wastewater ordinance [36] 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 [37]. 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 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 [38]. 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 [34], 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 [38]. In Sweden, WET is applied for monitoring purposes by the SE-EPA [39,40] as well as in the development of a monitoring program for the assessment of sewage effluent [41]. 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 [33].

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

This Appendix summarises information from the EU-RAR on sodium hypochlorite [1]. 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 2.3.2 of the main text. 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 4: 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 g/L

A6.2 Sewage treatment (PT2)

A6.2.1 Occurrence of DBPs

In the EU-RAR [1], sewage treatment is the use type that is considered to be most representative for 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 [4,6,7,15,42]. 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 [42]. According to the EU-RAR [1], there have been relatively few attempts to identify and quantify these in relation to typical operating conditions. According to the Euro Chlor document [6], 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 [7,15]. The EU-RAR refers to a study performed by WRc in 1993 for the UK National Rivers Authority [43] 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 [1,6]). 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. 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 [1], 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, viz:

- 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):

- 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 [1], "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 [9,17,18], 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 [17]. 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 5: Measurement of by-products of hypochlorite application in cooling water of coastal power stations, summarising data from Jenner et al. 1997 [17]

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. [17] 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, [9]), 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 [4,10].

Table 6: Formation of THMs upon chlorine treatment of cooling water at different sites. Table from [9].

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 [9], 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 7: Bromoform, chloroform, EOX and AOX in cooling water from different (industrial) locations. Translated copy from [9]

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 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) [18] 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.

A6.3.2 Risk assessment

In the EU-RAR, 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 section 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, 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 2.3.5.1 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 [9]. 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 [1]. 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. [43]. 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 section A6 2.3.

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