



SCIENCE DOSSIER | *John Pickup*

ENVIRONMENTAL SAFETY OF
HALOGENATED ORGANIC BY-PRODUCTS
FROM USE OF ACTIVE CHLORINE



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Environmental safety of halogenated by-products from use of active chlorine

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The author

John Pickup, who qualified as a chemist, spent over 20 years in the chemicals and detergents industries before establishing in 1994 a consultancy specialising in scientific issues, particularly the human and environmental safety of chemicals and downstream products.

The environmental impact of by-products of active chlorine use has been an ongoing focus of his consultancy work since its inception and he was heavily involved in dealing with that topic during the EU Risk Assessment of sodium hypochlorite

Environmental safety of halogenated by-products from use of active chlorine

Introduction

Apart from their use in chemical synthesis, active chlorine solutions have a wide range of applications ranging from purification of water for drinking, swimming and cooling to cleaning, bleaching and disinfection. Generally these applications make use of the powerful oxidizing properties of these solutions, and most of the organic matter with which these solutions react during use is oxidized by incorporation of oxygen, dehydrogenation etc. A small part of the active chlorine, however, can take part in chlorination reactions which create halogenated organic by-products.

The nature, properties and environmental fate of these by-products have been of particular interest to environmental scientists and regulators. This was initially because of concerns that they may include, or be similar to, some environmentally hazardous persistent, bioaccumulative and toxic molecules, such as the halogenated dibenzo-dioxins and -furans, and polychlorophenolics that were formed when chlorine gas or sodium hypochlorite were used to 'bleach' paper pulp. Although it was at one time suggested that halogenated carbon did not occur in nature, several thousand naturally occurring organohalogens have now been identified. Indeed, some millions of tonnes per annum of the smaller such molecules are formed as part of the earth's natural chlorine cycle.

This dossier reviews the nature and environmentally relevant properties of the by-products formed during current, non-reagent uses of active chlorine solutions. It addresses both the main chemical families of the by-products and the many minor components including often uncharacterisable halogenated macromolecules that make up the balance of the effluent mixtures. It considers the quantities of halogenated by-products typically produced during the various uses of active chlorine solutions, and the quantities likely to be discharged to the aquatic environment, and assesses their potential impacts on the aquatic environment.

1. Chemistry of reactions between active chlorine and organic matter

Active chlorine solutions, whether created from sodium or other hypochlorites, or from chlorine gas, comprise one or more of three different species – molecular chlorine (Cl_2), undissociated hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) – depending on the pH of the solution. As indicated in Fig 1 below for a 0.1M solution, Cl_2 is present only when pH is below 4. Between pH 4 and 5 the solution contains only HOCl , but as pH rises above 5 this increasingly dissociates forming hypochlorite ions: by pH 7.5 the solution contains similar amounts of HOCl and OCl^- and by pH 11, the normal pH of commercial sodium hypochlorite solutions, chlorine is present exclusively as OCl^- .

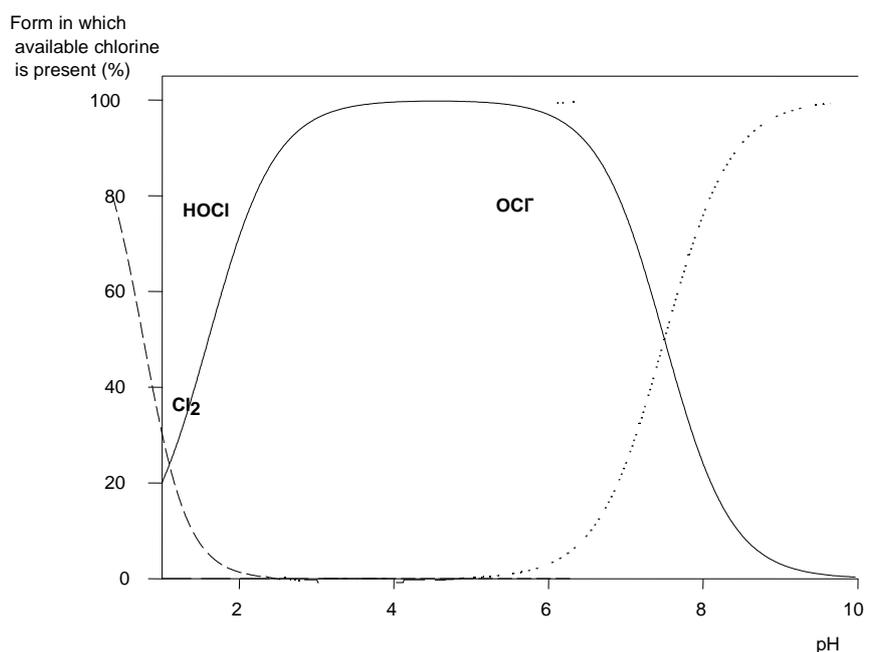
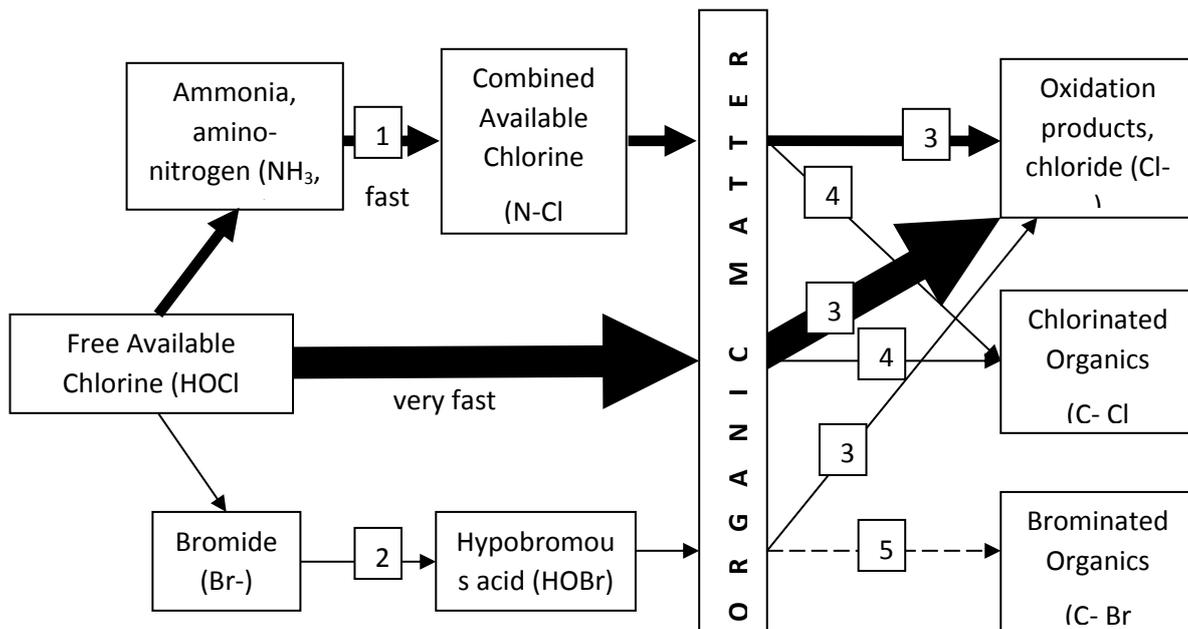


Figure 1. Calculated variation in composition of a chlorine solution with degree of acidity or alkalinity for 0.1 M Cl_2 in water at standard temperature and pressure. (The data in this figure are based on general chemistry handbooks).

Similar principles apply when the active chlorine originates from other releasing agents such as chlorinated isocyanurates, though a certain portion will remain as a 'reservoir' combined in equilibrium with various chlorinated and unchlorinated isocyanurates. For the purposes of this discussion, free active chlorine will behave similarly irrespective of source, though reaction rates may in some cases be slower: production of by-products from e.g. the chlorinated isocyanurates is not expected to be greater than that arising from inorganic forms of active chlorine. [WHO 2004]

Almost all current uses of active chlorine, from drinking water, swimming pool and sewage disinfection to cleaning and hygiene uses and cooling water treatment take place at neutral to alkaline pH. In these uses, the species reacting with organic matter are thus HOCl and/or hypochlorite ions. The former use of chlorine gas or hypochlorite in paper pulp bleaching at acid pH, in which Cl_2 was the active species, gave rise to a substantially different set of halogenated by-products.

The reactions of free available chlorine with organic matter are set out schematically in Fig 2 below:



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 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].

The principal families and types of halogenated by-products formed during use of active chlorine solutions can be summarized as follows:

- Trihalomethanes (e.g. chloroform (CHCl₃))
- Halocarboxylic acids
- Haloaldehydes
- Haloketones
- Halonitriles
- Halophenols
- Miscellaneous small molecules (CNCl, chloropicrin)
- Halogenated macromolecules (e.g. halogenated proteins, carbohydrates)

The quantities and concentrations in which each of these types is formed, and which of the individual members predominate, depends on several factors. These include pH, temperatures and reaction times, Cl:C ratios, presence of amino-nitrogen or bromide, as well as the nature of the organic substrates themselves.

It is important to note that the halogenation reactions that take place do not produce exclusively stable products that undergo no further change: on the contrary, especially in systems where a constant 'residual' of active chlorine is maintained, initial products react further. The general tendency is that the organic chlorine progressively becomes converted by further chlorination, hydrolysis, or oxidation to a limited range of more stable molecules, notably trihalomethanes and haloacetic acids. In water distribution mains, for example, the types and levels of by-products rise and fall according to residence time, temperature etc. Some by-products are volatile and are lost by evaporation, before or after release in effluents, while others hydrolyse, or biodegrade extensively in sewage treatment. The assessment of the potential environmental impacts of the ultimate effluents in the later sections of this dossier is thus not as complex as might at first be expected.

Effects of pH

The pH during use of active chlorine solutions will affect both the nature of the chlorinating species [see Fig 1 above] and sometimes the structure of the substrate. In almost all current uses, reactions take place at neutral to alkaline pH where the active chlorine is present as HOCl and/or OCl⁻.

At acid pH, however, active chlorine is substantially in the form of molecular chlorine (Cl₂). It has been observed that electrophilic substitution of Cl into aromatic substrates such as anisole (methoxybenzene) is acid-catalysed, which can increase both the extent of chlorination and the degree of substitution to form polychlorinated aromatics [Lebedev 2007]. It has been suggested that a hydrogen-bonded complex of HOCl with H₃O⁺ and H₂O is the reactive entity [Lebedev 2004].

Where suitable substrates are available, as for example in the former use of chlorine gas or hypochlorite for bleaching woodpulp, this can lead to the formation of polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs). Thus PCDD/F formation was observed in the chlorination of wood pulp at pH3, but above pH6 the amounts became undetectable (Hise 1989, Berry et al 1989). Similarly, polychlorinated compounds were not formed at or above pH5 when the 0.3mM of the precursors dibenzo-p-dioxin or dibenzofuran were mixed with 60mM hypochlorous acid (4,470 mg/L as sodium hypochlorite) for 24 hours (Onodera et al 1989).

Within the neutral to alkaline range, the kinds of trends that occur in formation of OBPs as pH changes are most easily seen in drinking water chlorination. Trihalomethane formation tends to increase as pH increases [Pourmoghaddas & Stevens 1995, Carlson & Hardy 1998]. Formation of haloacetic acids shows different trends: early work [Reckhow & Singer 1984] suggested TCA formation peaked at pH5, decreasing with increasing alkalinity through the typical water treatment range.

Pourmoghaddas & Stevens also found declining haloacetic acid formation as pH increased from 5 to 9.4, though the patterns became more complicated in waters with a high bromide content. Carlson & Hardy, comparing five different source waters, also found more complex patterns, still with an apparent pH maximum at 6.5 – 7.5, which they suggested reflected changes in the state of precursor material rather than shift of chlorinating species from HOCl to OCl⁻.

Total organic halogen, measured using the TOX technique, also tends to decline with increasing pH: a greater proportion of the TOX also becomes accounted for by THM and HAA, consistent with the more rapid hydrolysis of many halogenated by-products at higher pH [Singer, 1994; Pourmoghaddas & Stevens 1995].

Substrates

The range of possible organic reaction partners in uses ranging from drinking water disinfection to domestic and industrial cleaning and sewage treatment may seem infinite, and a source of great variability. Indeed substrates such as natural organic matter are themselves so complex that it is very hard to characterise them as discrete substances. At another level, however, the reaction partners also have much in common. The dominant substrates in many uses are the major components of biological systems i.e. proteins, carbohydrates and fats. Humic and fulvic substances present in natural waters will also be common to several use scenarios.

The major substrates in the former use in bleaching wood-pulp included cellulose and lignin, the latter rich in phenolic structures: while these will sometimes be present in some other uses, the reaction conditions, notably pH, mean that the latter especially is not extensively degraded or chlorinated in the same pattern.

Reaction times and temperature

Increasing reaction times and temperatures tends to increase the formation of OBPs as kinetics would predict. Numerous studies have been made of such effects in drinking water chlorination where optimisation of contact time is a key parameter for controlling by-product formation without compromising disinfection. Extending reaction times favours the production of the more stable small molecules, as decomposition reactions will also accelerate: as with increasing pH, as TOX increases an increasing proportion is thus made up of the major by-products THM and HAA [Pourmoghaddas and Stevens 1995, Carlson & Hardy 1998, Singer 1994]. Such effects are one reason for the seasonal fluctuation in by-product levels and composition in chlorinated tap water, though substrate changes are also a major influence. Similarly, by-product formation during short duration cleaning tasks conducted mainly at ambient temperatures, such as surface cleaning, is much lower (~0.1% of available Cl, [Josa et al 1997] than where contact is longer at higher temperatures, as when used to bleach laundry during machine washing (0.7 – 4%, [Smith 1994]).

It is also apparent that THMs and HAAs can form at noticeably different rates from different groups of precursors, sometimes distinguished as “quick formers” (resorcinol) and “slow formers”. [Pourmoghaddas and Stevens 1995, Carlson & Hardy 1998, Gallard & von Gunten 2002]

Active chlorine dose and Cl:C ratio

Increasing chlorine dose, and thus the ratio of active chlorine to organic substances available for chlorination similarly drives reactions further to completion and favours production of small stable by-products such as THMs and HAAs [Peters 1991]. However, Carlson & Hardy, studying chlorination of a range of source waters, found that while THM formation increased strongly as Cl:TOC ratios were brought up to 1, they levelled out thereafter. HAA formation continues to increase such that higher active chlorine doses effectively favour HAA formation over THM. Increasing chlorine dose also increases the formation of TCA over MCA and DCA, and chlorinated HAAs rather than brominated ones [Singer 1994], though it should be noted TCA tends to arise via separate precursors and pathways to DCA rather than forming directly from DCA by further substitution [Xie, 2003].

Increasing chlorine dose and Cl:C ratio will also increase the degree of substitution of aromatic substances, notably phenolics that occur in various forms of natural organic matter [Patnaik et al 2000], though in some such molecules (e.g resorcinol) the aromatic ring is cleaved and chloroform is the end product [Boyce & Hornig 1983].

Presence of amino-nitrogen

As noted earlier, presence of ammonia, ammonium ions or other amino-nitrogen atoms leads to rapid, and essentially quantitative, formation of inorganic and organic N-chloramines [Newell 1976; Weil & Morris 1949; Morris 1967; Margerum et al 1979]. The effect is to substantially reduce the formation of compounds containing carbon-chlorine bonds, and particularly the formation of trihalomethanes [Amy, Greenfield and Cooper 1990]. This led to chloramination (combined, sometimes sequential, use of active chlorine and ammonia) being increasingly adopted for water disinfection to achieve compliance with regulatory limits introduced for THMs. Most of the chloramines initially formed, notably monochloramine, are labile, however, and can react subsequently given long contact times to produce OBPs.

Similar observations have been made regarding chlorination of wastewaters. Chlorination of effluents which had been nitrified to remove ammonia produced higher quantities of OBPs than normal effluents containing ammonia [Rebhun et al 1997].

Presence of bromide

Bromide ion is commonly present at low levels in freshwater but can be present at higher levels in certain waters depending on geology, notably proximity to salt deposits, and of course in marine and estuarine waters. Active chlorine rapidly oxidises bromide to hypobromous acid (HOBr) and hypobromite ion, which exist in an equilibrium analogous to HOCl and ClO^- . One effect of this is that bromine competes with chlorine in substitution reactions such that fully or partially brominated organics additionally become part of the by-product mixture.

HOBr and OBr^- have also been found to be more efficient in substitution reactions than HOCl and OCl^- [Westerhoff et al 2004] such that the quantities or concentrations of brominated species formed can be somewhat greater and they can account for a larger fraction of the OBPs than would be indicated by the Br^-/Cl^- ratios. Chlorination of seawater used for cooling produces predominantly brominated, rather than chlorinated, organic by-products [Jenner et al 1997]. Formation of brominated THMs in particular, and to some extent HAAs, is favoured and proportionately more of the brominated by-products formed in drinking water are THMs or HAAs, compared to the chlorinated products [Pourmoghaddas and Stevens 1995, Qi et al 2004], though the relative instability of certain brominated species would also contribute to this.

2. Main halogenated by-product families and their environmentally-relevant properties

As noted earlier, the trihalomethanes and haloacetic acids are the halogenated by-products formed in the greatest quantities in essentially all current uses of active chlorine. They are commonly present at an order of magnitude greater concentration than the 'second tier' by-products, the haloacetonitriles, haloaldehydes, haloketones and halophenols. Accordingly there is much more data available on the both on the formation and the environmentally relevant properties of the former two families.

Trihalomethanes

All four trihalomethanes based on chlorine or bromine i.e. chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), chlorodibromomethane (CHBr_2Cl) and bromoform (CHBr_3) can be formed during various uses of active chlorine solutions. However, in most scenarios, where bromide concentrations are low, chloroform is the dominant THM, commonly accounting for >90% of total THMs, and the concentrations of the others usually decrease in the order $\text{CHCl}_3 > \text{CHBrCl}_2 > \text{CHBr}_2\text{Cl} > \text{CHBr}_3$ [Krasner 1989].

All 4 THMs are volatile with relatively low solubility in water, both volatility and solubility decreasing in the same order $\text{CHCl}_3 > \text{CHBrCl}_2 > \text{CHBr}_2\text{Cl} > \text{CHBr}_3$. Octanol/water partition coefficients range across this series from 1.97 (CHCl_3) to 2.4 (CHBr_3).

THMs are relatively recalcitrant to aerobic biodegradation, though all, and especially the more brominated members, degrade extensively in anaerobic conditions [Chloroform RAR].

As a result of these closely similar properties, THMs behave similarly in effluents and share a similar environmental fate. They are extensively removed from effluents and sewage by volatilisation. For example, chloroform is calculated to partition over 99% into sewer atmospheres [Zok et al 1998] and monitoring studies support such extensive transfer [Haas & Herrmann 1996]. THMs will be removed from effluents during sewage treatment by volatilisation rather than biodegradation, and stripping rates greater than 90% have been reported for chloroform [CHCl₃ RAR].

Hydrolysis of THMs takes place at alkaline pH, but at environmental pH the rates are sufficiently slow that calculated half-lives exceed 1000 years. Calculations suggest partitioning to sediments should be very limited [Zok et al 1998], and this appears to be borne out by monitoring data [Environment Canada, 1999; Environment Canada & Health Canada, 2001.]

As regards atmospheric impacts of volatilised chloroform, the EU Risk Assessment for chloroform comments that the global warming potential of chloroform is low and the substance is not classed as a greenhouse gas under the Kyoto protocol. It is not expected to be an effective agent of stratospheric ozone depletion and its contribution as a VOC to low-level ozone is considered negligible. [Chloroform RAR]

Extensive ecotoxicological data is available for chloroform [e.g. Zok et al 1998, Chloroform RAR]. Chloroform is moderately toxic to aquatic organisms, especially at the embryo/larval stage of development. Its aquatic toxicity is suitably characterised by the following long-term NOECs:

- Fish : NOEC-6/9 months : 1.463 mg/L (*Oryzias latipes*, Toussaint et al. 2001)
- Invertebrate : NOEC-21d : 6.3 mg/L (*Daphnia magna*, Kühn et al. 1989)
- Algae: 72h-EC 10 : 3.61 mg/L (*Chlamydomonas reinhardtii*, Brack and Rottler 1994)

A PNEC for aquatic toxicity of 146 µg/L may thus be derived by applying an assessment factor of 10 to the lowest NOEC [Chloroform RAR].

Several studies provide data on the brominated halomethanes as well as chloroform: data on bluegill (Anderson & Lusty 1980, Buccafusco et al 1980), carp embryos (Trabalka et al 1981, Mattice et al 1981) and daphnia magna (Le Blanc 1980) all show similar values for the various trihalomethanes suggesting the PNEC for chloroform would serve as a first approximation.

Haloacetic acids

Each of the nine different chlorinated/brominated acetic acids can be formed during use of active chlorine solutions, though dichloro- and trichloroacetic acids generally dominate except, as for the THMs, when there are substantial bromide concentrations present. In chlorinated drinking water the most common haloacetic acids are considered to be MCA, DCA, TCA, MBA, DBA and bromochloroacetic acid, sometimes collectively measured and expressed as HAA6. (An earlier, but still commonly used measure e.g. in US drinking water regulation is HAA5 which excluded BCAA as analytical methods for this were not then fully developed.)

The patterns that can occur are illustrated by the results of a survey of 35 Finnish waterworks using a variety of treatment technologies which found that DCA and TCA accounted on average for 35% and 49% of HAA6 respectively. However, in water from one works using a high bromide source DBA, BCA and DCA were the most common accounting for 44%, 31% and 18% of HAA6 respectively [Nissinen et al].

Haloacetic acids are relatively polar, non-volatile, water soluble species. Solubility in water at normal temperatures is of the order of 1,000 g/L for TCA increasing to 6,000 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 [HSDB].

The haloacetic acids are to varying degrees biodegradable, the most recalcitrant being trichloroacetic acid. Monochloroacetic acid is shown to be readily biodegradable, removal of 60-70% being achieved 10-14 days in tests conducted according to OECD Guidelines 301B-E. Inherent biodegradability tests show MCA to be nearly 100% biodegraded in 6-28 days. MCA is also extensively mineralised in anaerobic degradation tests. [MCA RA]

Trichloroacetic acid, in contrast, showed only 5-10% removal in 27 days in a Zahn-Wellens test for inherent biodegradability, but up to 46% removal in a modified MITI-II test (with 100 mg/L instead of 30 mg/L substance; 100 mg/L inoculum). Despite these test results, substantial removal of TCA is observed in monitoring studies. In five domestic sewage treatment plants in Switzerland removal ranged from 24-90% with an average of 66%. [OECD SIDS TCA]

The comparative degradability of the other chloro- and bromoacetic acids is illustrated by a study in which samples were incubated in river water for 30 days at 20 deg C in the dark [Hashimoto et al]. The six brominated acids and MCA were removed to below detection limits, in each case less than 1% of initial concentration, whereas 2% DCA remained and TCA was unchanged. Similar results were obtained incubating samples in seawater in the dark at 20deg C for 9 days, although TCA showed some reduction in this case (10-15% removal). By using HgCl₂ to inhibit bacterial activity in some samples the authors were able to attribute around half of the removal to biodegradation.

They also note various studies showing the HAAs are degraded by haloacid dehydrogenase enzymes produced by bacteria. Studies using field aquatic microcosms and simulated pond systems, however, found that while trichloroacetic had the longest residence time (~40 d), dichloro had the shortest (~4 d), and monochloro had an intermediate residence time (~14 d). Laboratory studies suggested that the biodegradation of trichloro-, dichloro-, and monochloroacetic acids leads primarily to the formation of chloride and oxalic, glyoxalic, and glycolic acids, respectively [Ellis et al 2001]. Tribromoacetic acid has been reported to spontaneously decompose in aqueous solution forming bromoform [Heller-Grossman 1993].

Haloacetic acids are substantially more toxic to algae than to zooplankton and fish, though recent studies have shown that algal toxicity of TCA is not as extreme as some data had previously suggested. Most information is available on mono- and tri-chloroacetic acids, though in general terms the toxicity of dichloroacetic acid tends to lie between these two. An overview of ecotoxicity data for the chloroacetic acids, from the selected key sources listed below, is set out in Table 1:

Table 1 Overview of aquatic toxicity data for chloroacetic acids

Toxicity mg/L	Fish		Invertebrates		Algae		Macrophytes	
	Acute LC50	Chronic NOEC	Acute LC50	Chronic NOEC	EC50	NOEC	EC50	NOEC
MCA	> 100 – 369	12.5 - 320	68.9 - 427	32	0.025 – 1.8	0.005 – 0.13	5.8 – 23.5	2.5 – 10
DCA					28.1	<1	47.3 – 722.5	3 - 300
TCA	2000 – 10000	7	2000 - >10000	-	16.2 - >115	3 - >115	49.5- 1702.6	3 - 1000

A fuller inventory of data is recorded in the EU Risk Assessment for MCA, the OECD SIDS for TCA and a review of the ecological effects of TCA by Lewis (2004). Hanson and Solomon (2004a, 2004b) studied macrophyte toxicity and assessed associated environmental risks.

The data for algal toxicity of TCA taken as the basis for calculating an aquatic PNEC for TCA in the OECD SIDS assessment were from a study by Bednarz [1981] which reported a NOEC for a strain of *Chlorella* of 8.7 µg/L, suggesting TCA had effects on algae at similar levels to MCA. When this value was subsequently used in assessing potential risks to the aquatic environment of haloacetic acid by-products during the EU Risk Assessment of sodium hypochlorite, it became apparent from algal toxicity tests on whole effluents containing TCA that this value was questionable.

Studies were thus repeated, under GLP conditions, on several strains of *Chlorella*, including the original strain used in the Bednarz study as well as on standard strains including those used for the whole effluent testing.

These studies [Roberts et al 2010] confirmed previous levels of toxicity for MCA but failed to reproduce the findings of Bednarz in respect of TCA. The most sensitive species of algae were standard species used in regulatory assessments, *Pseudokirchneriella subcapitata* and *Scenedesmus subspicatus* (NOEC 3 mg/L) while the *Chlorella* species tested were much less sensitive (EC50 >10 - >115 mg/L). The authors thus concluded the toxicity of TCA to algae is two orders of magnitude less sensitive than reported in the OECD SIDS. They suggest a PNEC of 0.3 mg/L applying an assessment factor of 10 (as used in the EU Hypochlorite Risk Assessment).

Brominated acetic acids appear to be somewhat less toxic to algae than the chlorinated equivalents [Kuhn & Pattard 1990, Unilever 2005].

Substance	End point	Toxicity µg/L
Monochloroacetic acid	EC50 biomass	28
Monobromoacetic acid		200
Monochloroacetic acid	EC10 biomass	7
Monobromoacetic acid		20
Monochloroacetic acid	EC50 growth	70
Monobromoacetic acid		1400
Monochloroacetic acid	EC10 growth	14
Monobromoacetic acid		100
Sodium dichloroacetate	NOEC	<1
Dibromoacetic acid		3

Haloacetonitriles

The four haloacetonitriles most commonly reported as by-products of active chlorine use are dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), chlorobromoacetonitrile (CBAN), and dibromoacetonitrile. Others may well be initially formed. 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.

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 [Glezer 1999]. While monochloroacetonitriles are the most stable and brominated species are more stable than chlorinated, dichloroacetonitrile is normally the most abundant of the group in chlorinated drinking water, though dibromoacetonitrile predominates where there are high bromide levels. Dichloroacetonitrile, for example, in effluents would be expected to be removed from receiving waters by both hydrolysis and evaporation, between 10 and 60% being lost by hydrolysis in 10 days at a pH of 6-8 and 50% estimated to be removed from a model river by evaporation in 10 days.

Haloacetonitriles would be expected to be relatively biodegradable and being water soluble (estimated log K_{ow} s <1), not to absorb to suspended solids or bioaccumulate.

Haloacetonitriles in effluents would thus be expected to be removed extensively in sewage treatment and levels in receiving waters would decline quite rapidly through a combination of processes.

Haloaldehydes

Chloral hydrate (trichloroacetaldehyde) has long been recognised as a by-product formed during use of active chlorine in drinking water and swimming pools for example, levels commonly being an order of magnitude below THMs and HAAs, though they can be higher in specific conditions. Recently, improved analytical techniques have also allowed measurement of brominated and lower chlorinated aldehydes. Laboratory data show haloaldehydes can be produced by chlorinating humic and fulvic acids [Miller and Uden 1983].

In drinking waters where chloroform is the predominant THM, chloroacetaldehydes predominate. Brominated variants increase as bromide content rises, though not to the same extent as with THMs. Dihalo derivatives seem to be present at lower concentrations than trihalo, though trichloroacetaldehyde can account for as little as 5% of haloaldehydes in some drinking water samples. [Koudjonou and LeBel 2006, Koudjonou et al 2008].

Haloacetaldehydes are not chemically stable in water at circumneutral pH and ambient temperatures. Koudjonou and LeBel found brominated derivatives were less stable than the chlorinated, and stability decreases as pH and temperature increases. At pH 7 and 22°C for example, half-lives of the trihalo species were around 4-6 days; at pH 8.2 and 22°C, the dihalo derivatives degraded between 20 and 88% in 2 days. Trihaloacetaldehydes hydrolyse to the corresponding THMs.

Haloaldehydes would thus be expected to be extensively removed from effluents and receiving waters by hydrolysis and evaporation of resulting THMs. The log K_{ow} of the most stable variant, trichloroacetaldehyde, is 0.99 indicating it should not bioaccumulate [CICAD Chloral Hydrate].

Haloketones

Various halogenated acetones and higher ketones may be formed during use of active chlorine. 1,1-dichloropropanone and 1,1,1-trichloropropanone are often the most abundant [Meier et al 1985]. Laboratory data show they can be produced by chlorinating humic and fulvic acids. Levels in drinking water, where reported, typically account for less than 1% of the total halogenated by-products and their formation decreases with rising pH and temperature, which may reflect transformation into other by-products [IPCS 216].

Haloketones tend to be hydrolytically unstable, their concentration in drinking water distribution systems often decreases sharply [Krasner 1989]. 1,1,1-trihaloketones undergo base-catalysed hydrolysis via the haloform reaction to form THMs. Haloketones are also relatively volatile; between 8-15% and 13-20% of 1,1-di- and 1,1,1-trichloropropanone respectively were observed to enter the vapour phase during operation of a test shower [Xu and Weisel 2003].

Haloketones would thus be expected to be extensively removed from effluents and receiving waters by a combination of hydrolysis and evaporation.

Halophenols

Chlorination of phenol in isolation in aqueous solution is a facile process. For example, Patnaik et al [2000] observed that phenol completely incorporates chlorine in dilute solutions. They found rapid initial reaction to form 2- and 4-chlorophenol within 1 min, followed by further chlorination producing 2,4- and 2,6-dichlorophenol and 2,4,6-trichlorophenol. Equilibrium was reached in around 15 mins at which stage the distribution of chlorinated phenols was as follows:

2-chlorophenol	20%
4-chlorophenol	22%
2,4-dichlorophenol	29%
2,6-dichlorophenol	7%
2,4,6-trichlorophenol	21%

The authors found that the stepwise addition of chlorine to chlorophenols was not as rapid as the initial chlorination of phenol, but the chlorination of the di-chlorophenols was more rapid than that of the mono-chlorophenols. No tetra- or penta-chlorophenols were detected in the product mixture reflecting the strong steric repulsion when three chlorine atoms are present.

Other phenols present in substrates may also potentially be chlorinated, though it should be noted that many phenols are also subject to ring-opening in neutral or alkaline solutions of active chlorine. Thus reaction of active chlorine with the complex phenolic structures present in humic material during chlorination of drinking water, for example, produces trihalomethanes and haloacetic acids as the major by-products and only very small quantities of chlorinated phenols.

Mechanisms stemming from 1,3-dihydroxybenzene structures, followed by ring opening have been proposed (De Leer et al 1985, Gallard and von Gunten 2002).

Chlorinated phenols are moderately to highly lipophilic. Successive chlorination of phenol for example raises log K_{ow} stepwise as follows:

Phenol	1.46
2-chlorophenol	2.15
2-6 dichlorophenol	2.75
2,4 di	3.06
2,4,6	3.69
2,3,4,6	4.45
Penta	5.12

[Data extracted from TOXNET Hazardous Substance Database, US National Library of Medicine]

Solubility in water at ambient temperature for this group ranges from around 25 g/L for 2-chlorophenol down to 14 mg/L for pentachlorophenol [Suntio et al 1988]. Chlorophenols are of limited volatility, decreasing with increasing molecular weight though their pungent odour and taste means even very low concentrations cause offence in drinking water. Volatilisation from receiving waters will be slow.

The lower chlorinated phenols are biodegradable in aerobic conditions, though sometimes requiring acclimation of the biomass to such substrates. As the degree of chlorination increases, aerobic biodegradability decreases, adsorption to sediments will increase, and anaerobic biodegradability will become the more important process.

Lower chlorinated phenols exhibit moderate aquatic toxicity, fish and daphnia apparently being similarly sensitive, with 96hr LC50 values in the range 2-8 mg/L for many mono-, di- and tri-chlorophenols. Tetra- and pentachlorophenol are an order of magnitude more toxic [HSDB].

3. Other halogenated by-products – trace and unidentified components

While many halogenated by-products formed during the use of active chlorine can be identified and grouped into the foregoing families, it is often the case that the sum of these components accounts for substantially less (sometimes even less than half) than the total apparently organically-bound halogen as measured using techniques such as TOX or AOX. This difference is probably most often due to the formation of sparsely chlorinated macromolecules from the naturally-derived organic matter present such as proteins, carbohydrates and humic and fulvic acids.

For example, Glaze et al (1979) observed that several high MW fractions (average molecular weight 2,500 – 19,000) from chlorinated lake water accounted for 260 $\mu\text{mole Cl/L}$ compared to 159 $\mu\text{mole Cl/L}$ accounted for by THMs, normally the largest group of halogenated by-products in such systems. The authors estimated that the average atomic ratio of chlorine to carbon in the high MW material was around 1:50.

Another potential factor in this difference is the formation of organic chloramines in which the carbon is bound to nitrogen rather than chlorine. Techniques such as TOX and AOX, although often regarded as measuring chlorine attached in C:Cl bonds, measure total contained chlorine after initial removal of chloride. While the chlorine in inorganic and small organic chloramines are normally sufficiently labile to be removed during sample preparation etc, chlorine attached in larger molecules, including chlorinated amino acids, peptides etc may be measured as organohalogens.

Trace components

In addition to the above, effluent mixtures after the use of active chlorine may also contain individually small amounts of a wide range of halogenated substances depending on the substrates originally present. Drinking water alone, for example, will contain thousands of different by-products, and the halogenated ones, some of them minor members of the groups considered above of course, may number some hundreds. Assessing potential environmental risk by assessing each individual component becomes impractical, and other approaches are required.

A good perspective on the overall risk can be gained by combining the conventional risk assessment of the major groups of substances firstly with an assessment of the environmentally relevant properties and ecotoxicity of the effluent mixtures (though this will also include the many non-halogenated by-products) and secondly with an assessment of the likelihood of formation of small, but significant, amounts of high-hazard substances.

1. Whole effluent studies

While the ecotoxicity of drinking water has received limited attention, whole effluents from cleaning uses of active chlorine were assessed in such a way by Ong et al (1996). They examined the biodegradability, bioaccumulation potential and ecotoxicity of effluents from washing machines in which hypochlorite bleach was added to the washwater containing dirty laundry and detergent to simulate household bleaching use. After elimination of unreacted hypochlorite with sulphite, they found that around 73% of the halogenated organics measured as AOX were degraded in a bench-scale activated sludge system. This was somewhat higher than the degradation of the AOX present (e.g. on laundry) in the effluent from a parallel machine run without hypochlorite.

The authors examined bioconcentration potential of the recalcitrant fraction of the washwater by HPLC. Numerous lipophilic substances were identified by mass spectrometry in both chlorinated and unchlorinated washwaters at the $\mu\text{g/L}$ level, but no substance containing chlorine was found in an examination of all peaks present at >100 ng/L . Tests on the recalcitrant fraction of the washwater on fathead minnow and *Ceriodaphnia dubia* showed the toxicity of the chlorinated washwater was similar to or lower than that of the unchlorinated washwater.

As part of the EU risk assessment of sodium hypochlorite, Johnson et al (2006) conducted a similar comparison of the biodegradability, potential bioaccumulation and ecotoxicity of substances in chlorinated and unchlorinated raw sewage. This was devised as a 'worst case' model effluent for by-product mixtures arising in a range of uses of active chlorine at alkaline to neutral pH, including potable, swimming and cooling water treatment and cleaning uses, as well as being a direct examination of by-products from sewage disinfection. The effluents were examined, following elimination of residual hypochlorite, for presence of substances that were both potentially persistent and bioaccumulative by degrading samples in a Zahn-Wellens test procedure followed by analysis of total organohalogen absorbed onto SPME fibres exposed to the samples.

No inhibition of biodegradability was observed in the Zahn-Wellens test. The chlorinated sewage sample prior to biodegradation showed elevated levels of chlorinated lipophilic substances detected via SPME fibre adsorption, but levels in the chlorinated sample after biodegradation were unchanged, indicating that any potentially lipophilic chlorinated substances were biodegradable. Tests on bacteria (Microtox), algae (*P. subcapitata*) and daphnia magna (14-day) showed no increase in acute or chronic toxicity between the (undegraded) chlorinated and unchlorinated samples.

The above studies indicated that halogenated organics formed during use of active chlorine at alkaline to neutral pH are extensively biodegradable, and found no evidence of formation of significant quantities of persistent, bioaccumulative substances. There were no indications of increased toxicity arising in the effluent mixture following chlorination.

2. Likelihood of formation of high-hazard molecules

While whole effluent studies find no indication of formation of significant quantities of persistent, bioaccumulative and toxic substances during use of active chlorine in neutral to alkaline conditions, some such substances were known to be formed during the former use of chlorine in acid conditions for bleaching paper pulp. Even small quantities of PBTs may become of concern if they build up in the environment over time.

Chlorinated organics are generally only likely to become simultaneously persistent and bioaccumulative when they have a high degree of chlorine substitution, as for example in tetra- or higher-chlorinated benzene rings, or in polychlorinated aliphatics.

Various organics can be polychlorinated to produce highly chlorinated organics in organic solvents, as used in organic synthesis, and polychlorination is observed to some extent in aqueous solution at acid pH such as in the processes formerly used for paper pulp bleaching. In neutral to alkaline aqueous solution, however, and with the substrate mixtures present in most current uses, polychlorination to produce highly chlorinated organics seems intrinsically unlikely: competing reactions such as oxidation or N-chlorination are very much more favoured and each successive chlorination of a given substrate normally becomes progressively more difficult.

One useful model that offers direct experimental evidence on this question is provided by the chlorination of phenol. Phenols are among the most readily chlorinated of all the molecules that may be present in sewage for which polychlorination could at least theoretically be postulated. Carlson et al (1975) examined the separate chlorination of various aromatics mono-substituted with activating groups towards electrophilic substitution of chlorine. The experiment was conducted in aqueous solution at pH 3, 7

and 10.1 using around 100 mg/L. Phenol incorporated chlorine most extensively (>97% uptake) at all pHs. At pH 3 some other molecules containing activating groups, such as anisole (80%) and acetanilide (55%), also incorporated chlorine extensively, while toluene (11%) and others containing deactivating groups (chloro, nitro, nitrile, carbonyl) incorporated much less (1-2%). At pH 7 only aromatics with activating groups incorporated chlorine (anisole 11%, acetanilide 3.4%, toluene 2.9%), and at pH10, where phenol still incorporated >97%, only anisole (2.8%) incorporated detectable amounts. The extensive incorporation of chlorine into phenol at alkaline pH reflects the particular reactivity of the phenolate anion.

The experiments of Carlson et al, and those of Patnaik et al were each conducted in aqueous solutions containing only the substrate. Thus they do not take account of competing reactions, such as oxidation or N-chlorination, which would be expected to take place in the presence of the wide range of organic matter and other substances seen in the sewage treatment and other scenarios. Though the chlorination of phenol in pure water is described as rapid, Lee and Morris (1962) found the reaction with ammonia to be 1000 times faster.

Various studies provide direct experimental data on the actual formation of chlorophenols in conditions typical of the use of hypochlorite in (waste)water treatment and cleaning scenarios. For example, WRc (Davis et al 1993) conducted studies on chlorination of raw sewage with hypochlorite. In typical conditions with moderate to high doses of hypochlorite (20 and 40 mg/L with and without 1 mg/L added bromide, stirred for 1 hour) they found no significant production of chloro or bromophenols. The suite of experiments included spiked samples to establish recoveries for phenol, four mono-, four di-, two tri- and two penta-halogenated phenols. These initial experiments found only the phenols below in the unspiked samples:

Concentrations in µg/L	Unchl.	20 mg/L		40 mg/L	
			+ Br ⁻		+ Br ⁻
Phenol	13.8	10.1	11.0	8.2	9.0
2-chlorophenol	nd	0.8	0.9	1.1	1.2
2,4-dichlorophenol	1.5	4.3	2.2	2.0	2.2
Pentachlorophenol	2.1	1.6	1.7	1.3	1.5

Subsequent experiments with “higher doses” of 40 and 100 mg/L available chlorine found the following:

	Unchl.	40 mg/L	100 mg/L
	Concentration µg/L		
Phenol	29.2	27.5	28.4
2-chlorophenol	1.6	7.5	17.9
4-chlorophenol	<0.1	2.4	4.5
4-bromophenol	<0.1	<0.1	3.3
2,4-dichlorophenol	<0.1	4.1	6.5
2,4-dibromophenol	<0.1	2.1	<0.1
2,4,6-trichlorophenol	<0.1	<0.1	5.6
Pentachlorophenol	<0.1	0.4	<0.1
Total AOX (duplicates)	289/166	458/673	984/1221

The remaining 5 halophenols were below the detection limit in all samples.

The authors comment that chlorophenol production did not appear to be limited by the availability of chlorine at realistic treatment doses (i.e. 20 – 40 mg/L) though it was increased at the higher 100 mg/L dose.

They suggested chlorophenol formation was not dependent on initial phenol concentration because phenol was being generated *de novo* from the action of chlorine on the humic material in sewage.

The halogen incorporated into halophenols (~4 / ~10 µg/L) represents only about 0.01% of the available chlorine applied, and about 1% of the organic halogen measured as AOX, at each dosage.

Thus, despite the facile chlorination of phenol in isolation by hypochlorite in aqueous solution, the amounts of halophenols produced in sewage chlorination, where there are abundant substrates for preferred oxidation and N-chlorination reactions, are very low.

Other authors have reported various chlorinated aromatics as minor components of the organohalogen mixtures formed during chlorination of wastewaters, or of substrates likely to be present in them (e.g. Jolley et al 1975, de Leer et al 1985). These are, however, generally restricted to monochloro- and some dichloro- derivatives e.g. chlorinated aromatic acids.

More detailed insight as regards aromatics less favoured than phenol for ring-chlorination is provided by a study by Reinhard et al (1976) who investigated the chlorination of the aromatic components of diesel fuel with aqueous hypochlorite at 100 mg/L for 1, 30 and 70 hours. The authors selected the aromatic components because they are more soluble in water and less resistant to chemical oxidation than aliphatic hydrocarbons.

One component of the fuel, 1,3,5-trimethylbenzene was found to react much more readily than the others, which the authors attributed to the effects of the three methyl groups m-substituted to each other combining to direct chlorination into the 2,4 and 6 positions.

Thus they found 30% of the 1,3,5-trimethylbenzene disappeared within 1 hr, whilst a peak corresponding to the monochloro- derivative had appeared suggesting mono chlorination. After 70 hours this was apparently converted into the dichloro- derivative. No formation of trichloro derivative was reported.

There was also some initial monochlorination of C2 naphthalenes after 1 hr but after 30 hrs these compounds had disappeared. No dichloro C2 naphthalenes were detected and the authors concluded the monochloro- compounds had been oxidised. Naphthalene, various methylindanes, phenanthrene and methylphenanthrenes showed no formation of chlorinated derivatives: some remained stable but others disappeared through oxidation.

The authors attributed the predominance of mono- rather than higher chlorination of the various aromatic substrates in diesel fuel to the deactivating effect of the chlorine substituent.

As regards the specific case of polychlorinated dioxins and furans, these can be formed by electrophilic chlorination in acid solution where chlorine (Cl₂) is present, but such formation is not observed in neutral to alkaline solution where the only species are hypochlorous acid and hypochlorite (cf Figure 1).

For example, polychlorinated dioxins form during acid chlorination of wood pulp at pH 3, but above pH 6 the amounts become undetectable (Hise 1989, Berry et al, 1989). Similarly, polychlorinated compounds are not formed at or above pH 5 when 0.3 mM dibenzo-*p*-dioxin or dibenzofuran is mixed with 60 mM hypochlorous acid (4,470 mg/L as sodium hypochlorite) for 24 hours (Onodera et al, 1989).

Various assessments made in respect of specific use scenarios at neutral to alkaline pH, outlined in the relevant sections below, have also found no indication or likelihood of

formation of dioxins and furans. Thus, the formation of significant quantities of highly halogen-substituted organics that might be persistent and bioaccumulative seems inherently unlikely in use scenarios where oxidisable substrates are present at neutral to alkaline pH, especially in the presence of amino-nitrogen containing compounds.

4. Halogenated organic by-products formed during various uses of active chlorine

The preceding section provides an overview of the range of halogenated by-products that can be formed in the use of active chlorine, and the factors that influence their formation. This section now examines in greater detail the types formed and the extent of their formation in the various different current uses of active chlorine, drawing both on studies of these uses and the preceding overview.

1. Water chlorination

Active chlorine is used to chlorinate water to control harmful or deleterious micro-organisms in three main scenarios: drinking water, swimming pools and cooling water. The concentrations of active chlorine used are low, pH is close to neutral, and while there are similar reaction substrates involved, such that the by-products formed are similar, there are also some significant differences.

a. Drinking water

Applied doses of active chlorine are typically below 5 mg/L, most of which disappears during oxidation reactions with organic matter to leave a residual normally around 0.1 – 0.5 mg/L free available chlorine.

The main organic reaction partners in raw water come from 'natural organic matter', much of which comprises the complex water soluble polymers referred to as humic and fulvic acids, which are rich in phenolic structures. Even so, the principal by-products formed are the trihalomethanes and haloacetic acids which will typically be an order of magnitude more abundant than the other main types, which include haloacetoneitriles, haloaldehydes, halo ketones. Levels of chlorinated phenols are low.

Since chlorination takes place at near neutral pH, formation of dioxins is not expected, nor is there good evidence to suggest that chlorination makes a significant contribution to normally low dioxin levels in drinking water.

The levels of by-products vary widely according to parameters such as raw water quality, pH, temperature, dose, contact time, treatment methods and sequence, and chlorination agent. Since the discovery of THMs in drinking water in 1974 [Rook], by-product formation has been intensively researched, and regulations applied in many countries to limit content [Roberson 2008, European Union 1998]. Novel techniques, such as 'chloramination', chlorination in the presence of added ammonia, have been introduced to reduce by-product formation.

New disinfection by-products at lower and lower levels are being discovered as analytical techniques advance. Krasner et al (2006) reported a range of more than 50 by-products in water treatment plants with high organic or bromide content. Plewa et al (2008) and Richardson et al (2008) for example have characterized and determined levels of haloacetamides and of iodinated by-products in US drinking water samples.

Much effort has also been devoted to trying to develop predictive equations which relate by-product formation to the above key parameters, though with limited success in terms of transferability between different geographical areas and water types. Chowdhury [2009] have reviewed the chronology and progress.

By-product levels also vary in the distribution system between the water treatment works and the point of use. Some by-products degrade in the pipes while others continue to be

formed from the small 'residual' of active chlorine which is maintained to inhibit microbial growth and maintain safety. The level of THMs, for example, which are the ultimate product of several reaction series, tend to increase, a 2-fold increase from works to tap being typical [Techware 1996]. HAA levels may rise but can also fall in mature water by hydrolysis and/or biodegradation within the pipes [LeBel et al 1997].

The situation in the late 1980s is perhaps suitably reflected in the figures below from a landmark paper by Krasner [1989]:

By-product type	Concentration µg/L Range of quarterly medians
Trihalomethanes	30 - 44
Haloacetic acids	13 – 21
Haloacetonitriles	2.5 – 4.0
Haloketones	0.9 – 1.4
Haloaldehydes (chloral hydrate)	1.7 – 3.0
2,4,6-trichlorophenol	<0.4
Total organic halide	150 - 180

The above ranges of medians will conceal wide variation in individual waters. One major determinant is whether the raw water is abstracted from the surface (rivers, lakes etc) or is 'groundwater' extracted from deep aquifers. Groundwater contains very low levels of organic matter and halogenated by-product formation is correspondingly low: trihalomethanes levels for example would normally be expected to be below 5 µg/L [Arora 1997]. Chloroform normally accounts for >90% of the THMs except where the raw water has a high bromide content.

DCA and TCA account, normally to a similar extent, for most of the haloacetic acid content, while MCA is usually very low. Total haloacetic acid levels are generally below THM levels in most situations, the ratio of HAA:THM typically being in the 30% - 70% range [Krasner 1989, Nieminski 1989, Villanueva et al 2003, Cancho et al 1999, LeBel 1997].

The situation can be different, however, where the raw water is derived from upland acid sources where there is an abundance of suitable precursors for haloacetic acids and levels can exceed THM levels, often by large margins. In a survey of Finnish waters by Nissinen (2002), for example, where HAA levels were undetectable in finished water from groundwater sources, HAA levels were uniformly higher than THM levels by a factor ranging from 1.5 fold to 67 fold, ranging up to 255 µg/L.

Similarly, Malliarou et al (2005) found that while mean HAA levels in UK potable water were 70% of THM levels in a lowland region (35.1 vs 50.9 µg/L), they were 3-4 times higher in a predominantly upland region (94.6 vs 27.6 µg/L) ranging up to 244 µg/L.

Nissinen et al highlight the effect of improved treatment techniques, contrasting the lower levels at works where these have been installed. These techniques, designed to control chlorinated by-products generally, but normally geared to THM standards, include physical organic matter removal, substitution of hypochlorite / chlorine in pre-treatment and use of chloramination to provide the disinfectant residual in the distribution system, In the 9 works which had applied combinations of the above techniques HAA levels ranged only between 6.4 to 36 µg/L. Bougeard et al [2010] similarly reported that although HAAs could be in excess of 100 µg/L in chlorinated upland waters in Scotland, plants using chloramination were below 80 µg/L.

Drinking water regulations in the USA regulate both THMs and HAAs: the stage 1 DBP regulations set a maximum contaminant level of 80 µg/L for THMs and 60 µg/L for HAAs (parameter HAA5 – the five most abundant acids). In stage 2, these levels would reduce to 40 µg/L for THMs and 30 µg/L for HAAs. Many EU countries have national

standards for THMs ranging from 10 µg/L measured at the works to 100 µg/L measured at the tap.

The EU Drinking Water Directive 98/83 limit established an initial limit of 150 µg/L at the tap effective end 2003 reducing to 100 µg/L THM limit by the end of 2008. In 2008, an EU standard of 80 µg/L for nine HAAs was proposed as part of a detailed review of Drinking Water Regulation in Europe in 2008. [Bougeard 2010, Cortvriend 2008]

As regards the distribution of halogenated by-products levels in drinking water around Europe, in 1997 approximately 57% of the potable water supply in the EU in 1997 was derived from groundwater sources in which THM levels would be expected to be below 5 µg/L. Haloacetic acid levels would be lower and other by-products an order of magnitude lower still.

As regards surface water sources, a survey for the EU [DG SANCO 2002a,b] found THM levels in seven different cities in six countries ranged up to 232.7 µg/L, with individual means of 3.5, 34, 35, 68, 76, 135 and 170 µg/L. With the Drinking Water Directive in full force, however, THM levels at the tap are required to be below 100 µg/L at all times suggesting a typical level no higher than ~70 µg/L.

In most circumstances, HAA levels would be a fraction of this, perhaps typically ~25 µg/L, though in water derived from upland sources without advanced treatment methods levels could be much higher.

b. Swimming pools

Swimming pools are chlorinated under closely controlled, often regulated, conditions to maintain a chlorine residual of around 0.4 mg/L free available chlorine and a pH between 6.5 and 8.5.

The pool water will contain halogenated by-products from the potable water used to fill it, but more are formed by reaction with both humic and fulvic substances in the water and organic matter introduced by swimmers in the form of sweat, sebum, urine etc containing a range of proteins, amino acids and fats.

The main halogenated by-products formed when swimming pool water is chlorinated are THMs, (mostly chloroform), di- and trihaloacetic acids with some smaller quantities of chloral hydrate and dichloroacetonitrile (WHO 2000).

In pool effluents the dominant compounds are DCA and TCA since the THMs tend to evaporate, and dichloroacetonitrile and chloral hydrate undergo hydrolysis to DCA and chloroform or TCA respectively.

The following analysis from a large outdoor pool in Barcelona, in which swimmer occupancy and chlorine dosing will be relatively high, illustrates the distribution of halogenated by-products present in the pool water [Univ Barcelona 1996].

(See table on next page)

By-product	Concn µg/L	Halide % Total
CHCl ₃	128	16.4%
CHCl ₂ Br	11	1.5%
CHClBr ₂	11	1.4%
CHBr ₃	21	2.8%
TTHM	171	22.1%
Chloral Hydrate	137	12.6%
MCA	2	0.1%
DCA	64	5.1%
TCA	436	40.6%
Total chloroacetic acids	502	45.8%
Trichlorophenol	<0.5	<0.1%
Total Organic Halide	699	80.6%

As the above illustrates, in swimming pools where the range of substrates is limited and plant-derived organic matter (humic material etc) is of less importance, a far greater proportion of the organic halide is accounted for by small, identifiable molecules since proportionately less will be part of sparsely-chlorinated macromolecules.

Swimming pool pH is controlled between 6.5 and 8.5 as noted above. Formation of dioxins is thus not expected.

c. Cooling water

Active chlorine is used to treat cooling water to prevent fouling by algae or higher organisms such as mussels, and growth of potentially hazardous micro-organisms. The largest systems treated, with the greatest potential environmental impact, are the cooling circuits of power stations, both those sited on freshwaters and coastal stations (including nuclear plants). In the latter case saltwater is taken in, chlorinated and discharged.

Chlorination may take place in a variety of regimes. 'Once-through' systems are often used for power plants on a preventative basis to inhibit macro-fouling. Even so, dosing of active chlorine is normally only continuous for short periods of the year, and intermittent or not applied for the rest. Typical levels may be 1.5 – 3 mg/L Cl, though somewhat higher levels are used to clean a fouled system. Recirculating systems are usually 'shock-dosed' at higher levels, ranging to above 10 mg/L when used once or twice per year, though lower doses may be used more frequently / continuously.

The main families of halogenated organic by-products formed during cooling water chlorination are THMs. These are normally the most prevalent, followed by haloacetic acids and haloacetonitriles. Halophenols are sometimes detected in limited amounts. Where the cooling water intake is seawater, as with large, coastal power stations the broad families of by-products formed are similar but brominated by-products predominate.

Berbee (1997) measured total THMs in water chlorination simulation studies on a variety of US river and lake waters. Chlorination at doses between 2.9 and 4.6 mg/L active Cl yielded THM levels between 4.7 and 30.7 µg/L. Chloroform accounted for the majority in most studies except one water with a high bromide level, where it accounted for 41%. In marine systems, Jenner et al (1997) measured bromoform and dibromoacetonitrile levels ranging from 0.72 – 29.2 µg/L and up to 3.15 µg/L respectively.

The main THMs and haloacetic acids formed in saltwater chlorination are bromoform and dibromoacetic acid. Khalanski (2002) found bromoform levels up to 26.8 µg/L and DBAA levels up to 10.19 µg/L in cooling water samples from three power stations. The most common halophenol found was 2,4,6-tribromophenol (mean concentration 0.25 – 0.29 µg/L, which was about 1% of bromoform levels) with only occasional detection of 2,4-dibromophenol (max 0.055 µg/L).

As noted earlier the environmental properties and toxicity of brominated and chlorinated species are similar, but the brominated oxidants formed are more reactive and have been observed to yield somewhat elevated levels of by-products, notably THMs, and to a lesser extent HAAs (Pourmoghaddas and Stevens, 1995). This may to some extent be counteracted because by-product formation will be somewhat reduced at the higher pH that is typical of seawater.

Seawater has a natural pH between 8.0 and 8.2, and the pH of freshwaters used for cooling will be kept close to neutral or alkaline to avoid corrosion problems or chlorine formation. In each case, dioxin formation is not expected.

2. Sewage disinfection

While hypochlorite is sometimes used *ad-hoc* to pre-treat sewage to control unwanted 'bulking' of micro-organisms in sewage treatment plants, disinfection of sewage effluent before discharge to receiving waters is sometimes a routine process. It may be applied either to secondary-treated effluent or, more rarely, to raw sewage e.g. for discharge to coastal waters without biological treatment. In some cases such treatment is required by local authorities, for example if the discharge is in the vicinity of a recreational water site.

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, and many different individual compounds have been identified in chlorinated sewage effluents.

Overall incorporation rates of applied available chlorine into chlorinated by-products, measured as AOX or DOX (dissolved organic halogen) are of the order of 0.5 – 2% depending for example on contact time and Cl:DOC ratio (Davis et al 1993, Rebhun et al. 1997).

It seems likely that most of the families of by-products produced during drinking water chlorination are also found in sewage. Trihalomethanes, particularly chloroform, and haloacetic acids predominate. The presence of ammonia in the effluent at low Cl:DOC ratios reduces the overall amounts of halogenated by-products formed including the THMs and HAAs but appears to widen the range of compounds formed (Rebhun et al. 1997). Sun et al [2009] however found HAA patterns in chlorinated wastewater changed rather than reduced, with a high prevalence of dihalo acids.

Focused experiments have shown that only small quantities of chlorinated phenols are formed in sewage chlorination, The phenols formed, were mainly 2-chloro- and 2,4-dichlorophenols: some formation of 2,4,6-trichlorophenol was observed only at high (100 mg/L) applied doses. Halophenols accounted for only around 1% of the total organic halogen formed and 0.01% of the chlorine applied (Davis et al 1993).

Dioxins are ubiquitous in sewage sludge samples, whether the sewage has been chlorinated or not. The levels and congener profiles vary widely showing a variety of sources. As chlorination takes place at neutral to slightly alkaline pH, no dioxin formation

would be expected during chlorination however. Although the possible sources of sludge dioxins have been extensively researched, there are no reports suggesting sewage chlorination makes a contribution. Household wastewater, which carries dioxins washed off contaminated textiles, has been identified as an important source for sewage works serving residential areas,

3. Domestic, industrial and institutional cleaning and disinfection

Sodium hypochlorite has been used for over a century in the home: its uses range from cleaning, removal of stains and mould and disinfection of household surfaces in such places as kitchen and bathroom surfaces, in the toilet and wherever hygiene is important. Though concern about possible environmental impacts and damage to soft furnishing through spillage have limited its use in recent years, it is extensively used in hospitals and other healthcare institutions, as well as in the food and catering industries, hotels and offices as well as in industrial laundries.

While product is occasionally used neat at a concentration of 3 - 5% e.g. for toilet cleaning, most uses are as dilute solutions, typically 0.1% for most domestic, institutional and industrial cleaning, but up to 1% for disinfecting particular pathogens in hospitals. These solutions invariably have an alkaline pH, ranging from 12 or above for neat product down towards neutral with increasing dilution.

Elevated temperatures, extended contact times or high Cl:C ratios, which may be encountered in some uses, will tend to increase by-product formation, particularly of small molecules. On the other hand, the high pH will tend to depress overall by-product formation.

The substrates encountered in these uses are generally a combination of natural soils comprising proteins, carbohydrates and fats. When disposed of to drain unreacted active chlorine in the cleaning solutions will encounter a large excess of amino-nitrogen rich raw sewage comprising similar constituents, and be rapidly destroyed. In laundry use, particularly in machines, surfactants and other components of detergents may also be present.

The formation of halogenated organics from the typical range of domestic bleach use has been directly examined in a field study in Italy where per capita usage of bleach is relatively high [Schowanek et al 1996]. The study recorded product consumption by around 420 people in several apartment blocks, and measured associated effluent levels. About 1.5% of the active chlorine used was converted to organohalogen measured as AOX. The AOX concentration arising was approximately 33% of the total in the domestic effluents, with around 14% coming from the tap water which, being from a groundwater source, had a low AOX content averaging 15 µg/L.

Within the range of tasks, laundry bleaching produces some of the highest observed Cl to AOX conversion rates: Smith (1994) found conversion rates of 0.7-4% during machine washing with detergent (6.2% in one sample). Interestingly, the detergent appeared not to contribute to AOX formation. In contrast, use of active chlorine for hard-surface and toilet cleaning produces lower conversion rates, the formation of OBPs during five different common tasks being measured as ranging from 0.06% (as AOX) of the active chlorine for toilet cleaning to 0.12% for floor cleaning (Josa et al., 1997). In these uses however, more OBPs are likely to be formed after spent cleaning solutions are released to mix with sewage when they are poured down the drain or when the toilet is flushed, though the active chlorine will be rapidly destroyed.

Smith (1994) found that the major classes of by-products formed during use of hypochlorite in machine laundry bleaching, were chloroform (average 10.3% of AOX), dichlorobromomethane (0.8%), trichloroacetic acid (5.2%) and dichloroacetic acid (6.2%). Dichloroacetonitrile, which was estimated to have a half-life of 6 mins in the prevailing conditions, accounted for a further 1.5% of AOX. Chlorophenols were not detected with a detection limit (30 µg/L for 2,4,6-trichlorophenol) equivalent to 0.4% AOX. In a similar study between 0.3 and 3.3% of the chlorine, added as hypochlorite, was converted into AOX, of which approx. 17% could be identified as chloroform (IVL, 1990).

All cleaning and disinfection uses of hypochlorite take place at alkaline to neutral pH, so formation of polychlorinated dioxins and furans is not expected. The presence of dioxins in municipal sewage sludge and household wastewater, prompted a series of studies looking for possible formation of such compounds through household use.

These studies examined hypochlorite use in the most aggressive conditions of household use i.e. in laundry and machine dishwashing, but they have concluded that this does not happen (Office of Nature Conservancy, Sweden, 1992; Rappe & Anderson 1992; Horstmann & McLachlan 1995). In each case dioxins were detected but the levels were similar whether hypochlorite was used or not. Subsequent studies showed that the dioxins found in household wastewater originate from certain contaminated textiles rather than from detergents, bleaching agents, or from the washing process, (Horstmann et al, 1992, 1993a, 1993b; Horstmann and McLachlan 1994a, 1994b, 1995a, 1995b, 1995c).

Since the major classes of halogenated by-products account for less than half of the total measured as AOX, some authors have examined biodegradability, lipophilicity and toxicity for the whole waste cleaning solution, again using washing machine effluent as the model. As noted above [section 3, trace, i].

Ong et al found 73% of the organic halide was degraded in a bench-scale activated sludge system. No chlorinated substance was found in an examination of all peaks present at >100 ng/L in an HPLC examination of the lipophilic fractions of the effluent. The authors concluded that use of hypochlorite in laundering is unlikely to generate persistent bioconcentrable compounds. Use of hypochlorite did not increase the toxicity of the effluent to fathead minnow or *Ceriodaphnia dubia*.

Braida et al (1998) studied elimination in model septic tank systems. Over 20 weeks rates of removal (87-94%) were observed. No accumulation of AOX in septic tank sludge, or on the sands and loams comprising the leach field, was observed during the course of the study.

4. Textile treatment

Active chlorine has been used for cotton bleaching for over two centuries, though this use now seems to be substantially discontinued. As cotton bleaching is conducted at slightly alkaline pH, no dioxin formation would be expected and studies by Horstmann et al (1993b) confirm this: they investigated polychlorinated dioxin and furan levels on cotton cloth through 16 different stages of textile processing and finishing. The dioxin levels on the samples after hypochlorite treatment, both with and without peroxide, were marginally lower than prior to those treatment steps.

One continuing use of active chlorine, for wool-shrinkproofing, does employ acid pH however. The sodium or calcium salts of the dichloro-isocyanuric acids are generally used for wool chlorination. In the continuous Chlorine Hercoset process, as it is known, chlorination under acidic conditions is followed by antichlor treatment to remove residual/unreacted chlorine. This prepares the wool for application of a chlorinated epoxide resin by producing negatively charged proteins at the surface of the fibre and generating a hydrophilic surface through removal of chemically bound fatty acid.

Chlorination is carried out at 10-15°C at a pH of around 1.5-2.0 such that the chlorine will be present as Cl₂. The chlorine reacts rapidly and virtually quantitatively under these conditions: any residual, unreacted chlorine is neutralised with sodium sulphite at 40°C and pH is adjusted to 9.

As wool is proteinaceous in nature containing amino acids and polyamide linkages, the amino nitrogens would be expected to be a favoured reaction site resulting in N-chloro derivatives rather than C-Cl bonds. During acid chlorination of wool soluble chlorinated proteinaceous material is formed. This is mainly responsible for the AOX load of the process effluent, though AOX can also arise after the hypochlorite stage from the application of an epichlorhydrin-based processing resin. Volatiles typically account for less than 5% of AOX in the total effluent. [Augustin 1991]

As wool bleaching takes place at acid pH, the possibility of dioxin formation arises. However, wool is proteinaceous and the phenolic dioxin precursors that are present in wood-pulp are not present. Measurable dioxin concentrations are present in the chlorination line effluent though it is not established whether they were formed during chlorination or whether they arose from some other source. This concentration is of a similar order to domestic washing machine effluent and to that found in municipal treatment plant influent, so process effluent would not significantly increase dioxin levels in sewage sludge.

5. Pulp and paper industry

Until recently there was a large scale use of chlorine / hypochlorite in acid conditions to 'bleach' wood or other pulps in the process of papermaking. The pulp as introduced to the bleaching stage typically contained 5% to 10% lignin, a natural polymer which contains complex phenolic structures.

In the first stage of bleaching, about half the chlorine applied to pulp combined with the lignin and the remainder oxidized the lignin and was converted to chloride ion (Kempf and Dence, 1970; Hardell and de Sousa, 1977). Of the applied chlorine, about 90% had been converted to chloride ion following the alkaline extraction stage; about 10% had been incorporated into organic molecules.

At acid pH elemental chlorine reacts with double bonds to produce dichlorinated products but at higher pH, towards neutral, hypochlorous acid predominates. This reacts differently with double bonds to produce chlorohydrins which release chlorine again in the alkaline extraction stage giving lower formation rates of chlorinated organics. Where chlorine dioxide is used, hypochlorous acid is generated in situ by reduction of chlorine dioxide as the lignin is oxidized.

The oxidised lignin contains fewer aromatic structures than lignin and less chlorinated aromatic material is formed. A 5-10-fold decrease in overall halogenated organics formation has been observed (Solomon et. al, 1993, McKague and Reeve, 1994).

The chlorinated organic material deriving from the pulp bleaching process was shown to be a complex mixture of different compounds, ranging from degradable to persistent and from relatively non toxic to more toxic. The range of low molecular weight substances included the trihalomethanes and some other chlorinated alkanes, chlorinated carboxylic acids and dichloroacetonitrile. Because of the high concentration of phenolic material and acid pH, a wide range of chlorinated phenols was formed, including chlorocatechols, chloroguaiacols, chlorosyringols and chlorovanillins.

There was also a range of highly lipophilic compounds including chlorinated resin acids, chlorinated dibenzothiophenes, chlorinated thiophenes, chlorocymenes, chlorocymenenes, chloronaphthalenes, chlorophenanthrenes and PCDDs/PCDFs.

The main surviving use of active chlorine in the paper industry (apart from equipment cleaning) is now in tissue mills to treat 'broke', rejected or waste tissue which is to be recirculated within the mill's production processes. Hypochlorite is used at an initial solution concentration below 100 ppm to break down resin added to tissue to improve its wet strength. This process takes place at alkaline pH, both for maximum effectiveness and because this also minimises degradation of the cellulose fibre. The hypochlorite readily reacts with the amide linkages in the resin and also oxidises and chlorinates azetidinium ring structures via a classic haloform reaction to form first alpha-haloketones and then chloroform [Chung 2003]. Chloroform and N-chloroamino- compounds are expected to be the dominant by-products.

In broke, which is fully processed and bleached pulp, levels of phenolic-rich lignin are low in contrast to raw pulp and since pH is always alkaline no formation of dioxins would be expected. Any chlorination of phenols would give mono- or di-chlorinated compounds rather than higher chlorinated analogues [Hise et al 1997]. Some chloroform may be produced by the slow reaction of active chlorine with cellulose [Hise 1995].

5. Risk assessment

The potential risks to the aquatic environment from organohalogen by-products likely to arise from current uses of active chlorine have been assessed in detail in the EU Risk Assessment of Sodium Hypochlorite under the Existing Chemicals Regulation. [Hypochlorite RAR]

Given the complex nature of the by-product mixtures often involved, the risks were characterized using a combination of several approaches:

- The risks from the major by-product families (THMs and HAAs) were characterized by conventional PEC/PNEC calculation
- Risks from minor halogenated by products were characterised semi-quantitatively by reference to the major families
- Whole effluent toxicity tests conducted on sewage treated with active chlorine served as a worst case model to assess the combined toxic effects of the range of by-products produced.
- Risks from possible formation of high-hazard molecules were assessed mainly qualitatively using quantitative data on formation where that had been detected.

Table 2 (below) summarises the local Predicted Environmental Concentrations (PECs) and Risk Quotients for THMs and HAAs determined by the EU Risk Assessment for different hypochlorite applications.

Active chlorine use scenario	Trihalomethanes		Haloacetic acids	
	PEC Local µg/L	RQ	PEC Local µg/L	RQ
Household Cleaning	0.11	0.0026	0.27	0.48
I&I Cleaning (Hospital scenario)	0.034	0.0021	0.086	0.24
Swimming Pool (Routine)	0.02	0.0020	0.16	0.33
Swimming Pool (Emptying)	0.67	0.0024	6.22	2.46*
Sewage disinfection	7.0	0.05	3.5	4.25
Textile processing	0.10	0.0025	0.21	0.39
Drinking Water:				
Groundwater	0.05	0.0022	0.04	0.19
Surface Water				
Good quality	0.35	0.0042	0.17	0.34
DWD THM compliant	0.70	0.0066	0.34	0.54
> DWD THM limit	1.70	0.0135	0.51 – 3.30	0.74 – 4.02
Upland (acid)			1.08 – 7.80	1.41 – 9.32
Paper broke re-pulping	14	0.098	1.25	1.61
Cooling water treatment:				
Seawater	0.3	0.004	0.1	0.26
Freshwater	3.0	0.022	1.0	1.32

The risk quotients calculated were arrived at using the following values:

		Source
THMs		
PEC regional	0.268 µg/L	EU Chloroform Risk Assessment
PNEC	146 µg/L	EU Chloroform Risk Assessment
HAAs		
PEC regional	0.12 µg/L	OECD SIDS Assessment
PNEC	0.85 µg/L	TCA NOEC 8.7 µg/L with AF=10

For THMs, the risk quotients in Table 2 (above) are low, all below 0.1 and often below 0.01 and the risk assessment conclusion accordingly is 'no concern'. Similar no concern conclusions were reached directly for about half of the HAA assessments. However, the risk quotients highlighted in bold are greater than 1 and would normally indicate a possible risk.

The risk assessment noted, however, that the NOEC for TCA was derived from non-standard tests using an obsolete and non-standard species (reported as *Chlorella pyrenoidosa*) and considered preliminary data available from the standard tests performed and subsequently published by Roberts et al [2010]. It also noted that algal toxicity was not seen in the whole effluent tests in which the haloacetic acid content would have been over an order of magnitude higher than this NOEC.

The assessment concluded that taking the above into account the overall weight of evidence also indicated no concern for these scenarios. The conclusion by Roberts et al that a true NOEC, and thus PNEC, for trichloroacetic acid, upon which the haloacetic acid PNEC was heavily based, is more than 300 times higher than the SIDS value shows this conclusion to have been sound.

Apart from THMs and HAAs, the wider range of small chlorinated molecules are typically present at one or more orders of magnitude lower concentrations. Although there was insufficient data to conduct individual PEC/PNEC calculations, it was considered the toxic effects were likely to be small compared to the THMs and HAAs. This view was supported by the whole effluent toxicity tests which found no increase in toxicity of the effluent following chlorination (after elimination of residual hypochlorite).

A review of the chemistry indicates that polychlorination to create highly lipophilic and persistent chlorinated organics is unlikely. This expectation was confirmed by the whole effluent tests. An increase in the level of chlorinated lipophilic substances was observed when sewage was chlorinated, though this is not unexpected since existing lipophilic species (e.g. unsaturated fats) are easily chlorinated. However, the level was not elevated when the chlorinated sewage sample was subjected to biodegradation indicating that no significant levels of persistent lipophilic substances were formed. This confirmed individual findings from prior experiments e.g. with washing machine effluents.

For each use scenario, the risk assessment specifically considered the likelihood of formations of high-hazard dioxins and furans. Since reactions in all except one use take place at neutral or acid pH, such formation was not expected and in some scenarios this had been positively confirmed by experiment. When hypochlorite is used in the textile industry for wool shrinkproofing, dioxins were detected in process effluents and formation could not be ruled out. However, the levels involved were low and of the same order as those typically found in domestic washing machine effluents (which are known to be from adventitious sources), and would not significantly increase sewage loads.

The EU risk assessment thus concluded that no significant environmental risks were expected from the uses of hypochlorite studied and no additional risk management measures were necessary.

6. Conclusions

During the various uses of active chlorine, which range from water treatment to cleaning, bleaching and disinfection, most of the applied chlorine is converted to inorganic chloride. Some chlorine, however, will react with the substrates present to produce a range of by-products including N-chloramines, and a variety of chlorinated organics containing C-Cl bonds. The quantities of chlorinated organics formed are generally small: the proportion of Cl incorporated is typically between 0.01 and a few per cent, though in clean systems such as drinking water treatment where C:Cl ratios are low up to 25% of applied chlorine can form C-Cl bonds.

The quantity, range and distribution of chlorinated organics formed depends on pH, substrates present, temperature, contact time and Cl:C ratios. The presence of amino-nitrogen (as ammonia, amino acids or protein fragments for example) leads to rapid formation of chloramines, which mainly decay over time to chloride though some will also form C-Cl bonds. Presence of reducing agents (e.g. ammonia, sulphides) favour rapid reduction of the chlorine to chloride. Other halogens present can also be incorporated: while chlorine normally accounts for >90% in systems with high bromide levels bromine containing organics can predominate. Iodine can also be incorporated but at orders of magnitude lower levels and iodo-halogen by-products are only now becoming studied in detail.

Almost all current uses of active chlorine take place at neutral to alkaline pH and the chlorinating species are HOCl and OCl⁻, the former predominating only close to neutral pH, the latter above pH 7.5. Throughout this pH range, the most common by-products are the trihalomethanes and haloacetic acids; normally these account for the majority of small halogenated organic molecules present.

THMs and HAAs are typically an order of magnitude more abundant in halogenated by-product mixtures than other families, which include haloaldehydes, haloketones, haloacetonitriles and, generally at low levels, halophenols. Where active chlorine comes into contact with substrates during use containing natural organic matter, such as fulvic and humic acids present in raw surface water, a significant proportion of the chlorine bonded to carbon is in the form of sparsely chlorinated macromolecules. Many halogenated by-products are not stable in water over time, particularly in the presence of active chlorine and reactions will progress to convert these molecules into the relatively stable trihalomethanes and di- and tri- haloacetic acids.

At neutral and alkaline pH, substitution of chlorine into aromatic rings is not favoured. Although mono- and di- substitution can be observed in certain molecules, especially where there are substituent groups that favour electrophilic substitution, steric hindrance inhibits further substitution. Moreover, while phenol can be chlorinated in isolation to give significant yields of tri- and higher chlorophenols, in actual use scenarios where oxidisable substrates and other preferred reaction partners are present, halophenol formation is very limited and polychlorophenols are not normally formed. Indeed, the complex phenolic structures in humic and fulvic acids undergo ring opening and onward reaction to THMs and HAAs during water chlorination with minimal halophenol formation.

In the light of the above, polychloro-dioxin and -furan formation would not be expected in neutral and alkaline conditions and experiments in various use scenarios have confirmed this does not occur.

At acid pH, the pattern of reactions of active chlorine with substrates is different. Electrophilic substitution into aromatic rings is acid-catalysed and correspondingly favoured. Consequently, the former use of chlorine or hypochlorite at acid pH to 'bleach' paper pulp gave rise to an array of chlorinated, including polychlorinated, aromatics, especially phenolics (given their abundance in lignin) as well as THMs and chlorinated alkanes, carboxylic acids etc. There was substantial formation of dioxins and furans.

In the one continuing use of active chlorine at acid pH, for wool shrinkproofing, the substrate is proteinaceous and the main reaction products appear to be N-chlorinated protein fragments and amino acids. In the absence of phenolic structures, dioxin formation would be expected to be limited and although it has not been ruled out the levels found in effluents are low and comparable to those adventitious amounts found e.g. during washing clothing.

The halogenated by-products formed during use of active chlorine at neutral and alkaline pH have a range of environmental hazards and profiles. The quantities of lipophilic and thus potentially bioaccumulative halogenated organics in by-product mixtures are limited: there will be some addition of chlorine to unsaturated fatty derivatives but few polychlorinated substances. Effluent mixtures after chlorination tend to be more biodegradable generally, probably reflecting breakdown of recalcitrant structures through oxidation. The C-Cl and N-Cl bonds present are relatively easily cleaved during biodegradation.

The potential environmental risks arising from current uses of active chlorine have been formally assessed in the EU Risk Assessment of Sodium Hypochlorite under the Existing Chemicals Regulation. The specific risks from halogenated organic by-products were assessed in detail using a combination of approaches and the conclusion reached for each use scenario is that with current risk management measures these by-products pose no significant risk to the environment.

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Other Euro Chlor Science publications

Focus on Chlorine Science

Electromagnetic fields in chlor-alkali production - Health effects and regulation – January 2009

Life Cycle Assessment – November 2006

Risk assessment and cycling of natural organochlorines – May 2006

Environmental fate and impact of chlorinated solvents – December 2005

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Key Science Information Sheets (KSIS)

Bioaccumulation – January 2005

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Dioxins – April 2002

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Children and exposure to highly chlorinated chemicals – August 2000

Science literature reviews

Bio-dehalogenation: Between 2001 and 2005, Professor James Field (University of Arizona, USA) provided Euro Chlor with quarterly updates of published scientific literature reporting on microbial (de)halogenations of key chlorinated compounds. There are 15 issues.

Natural organohalogens: From 1995 to 2002 Professor Gordon Gribble (Dartmouth College, Hanover, New Hampshire, USA) provided Euro Chlor with a series of periodic updates to the natural halogen literature, focusing on organochlorine compounds. There are 18 issues.

Marine Risk Assessments

1,2-Dichloroethane

1,1,2-Trichloroethane

Tetrachloroethylene

Trichloroethylene

Chloroform

Carbon tetrachloride

Dichloromethane

Hexachlorobenzene

Hexachlorobutadiene

1,2,4-Trichlorobenzene

1,1,1-Trichloroethane

Vinyl chloride

Monochloromethane

1,2-Dichlorobenzene

1,4-Dichlorobenzene

Mercury

Monochlorophenols (2-, 3- and 4-)

PCBs, DDT and dioxin

Pentachlorophenol

1,1-Dichloroethylene

Monochlorobenzene

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