

FOCUS ON CHLORINE SCIENCE

Chlorination by-products

Introduction: controlling microbes and cleaning

Chlorine, often in the form of sodium hypochlorite (eg bleach), is used globally to protect public health. As well as swimming pool disinfection, applications include: disinfecting drinking water and sewage; cleaning and disinfecting homes and hospitals; disinfecting processing equipment in the food and catering industries; preventing microbial growth in cooling water systems. The halogenated by-products (HBPs: eg chlorinated or brominated by-products) formed during these applications have been studied because of their potential toxicity and because some highly-chlorinated substances do not degrade easily. Examples of past and present concerns are respectively the formation of highly chlorinated hazardous molecules such as dioxins in paper pulp bleaching and inhalation of by-products by swimmers in public indoor pools.

When added to water of alkaline pH, chlorine becomes a solution of sodium hypochlorite known as 'active chlorine'. This cleans and disinfects by oxidising natural organic matter such as proteins, carbohydrates, fats and bacteria. The 'active chlorine' breaks down in the process almost entirely into chloride ions – effectively salt.

While the organic matter is broken down mainly into oxidised decomposition products, a small amount (1-2 %) of the chlorine forms carbon-chlorine bonds. This reaction creates a variety of chlorinated organic by-products. If there are substantial amounts of bromide ions present, as in sea water, some of these by-products will be brominated. In the presence of ammonia or amino groups, found in sewage, some inorganic and organic chloramines will initially be formed. These in turn decompose through oxidation reactions with the chlorine reverting to inorganic chloride.

Halogenated by-products

The halogenated by-products (HBPs) formed have been studied due to their potential toxicity and because some highly-chlorinated substances do not degrade easily. The nature of the HBPs formed depends on the types of organic matter and constituent molecules present, and the conditions in which the reaction takes place: pH, concentration, chlorine-to-carbon ratio, presence of amino compounds etc.

All uses of 'active chlorine' for microbial control and cleaning take place at alkaline or neutral pH. Here, the principal by-products are trihalomethanes (THMs; mainly chloroform) and haloacetic acids (HAAs), with smaller amounts of haloaldehydes,

haloacetonitriles and halo ketones. Normally, a significant percentage of the halogen is present in molecules that cannot readily be identified, often because these are macromolecules – fragments of organic matter such as protein or carbohydrate that are not themselves readily identifiable.

'Active chlorine' is sometimes used in a solid form e.g. as chlorinated isocyanurate compounds for private swimming pools or drinking water disinfection. The range of HBPs formed will be similar because the isocyanurates rapidly dissolve in the water forming hypochlorous acid and hypochlorite.

A major concern from the past in Europe was the formation of some highly-chlorinated molecules, such as dioxins, resulting from the

now abandoned practice of bleaching paper pulp with chlorine. However, dioxins were only formed from 'active chlorine' under specific conditions: acid pH and in the presence of certain phenols such as those abundant in the lignin component of wood. Dioxins form more readily when there are high chlorine concentrations, high chlorine to carbon ratios, and extended contact times. There is no significant formation of dioxins or other high-hazard molecules at neutral or alkaline pH adjustment; and chlorination in the presence of ammonia.

By-products formed in different uses

Disinfecting water with active chlorine to make it safe to drink provides low level 'residual' chlorine (0.1 – 0.5 mg/l active chlorine) in mains and pipes. This ensures water remains safe to drink right up until it comes out of the tap, even if the mains are not leak proof.

The HBPs formed in drinking water depend on the nature and quantity of organic matter present, as well as on the disinfectant and other treatments used. THMs and HAAs (mainly dichloro- and trichloro-acetic acids) typically account for 20-80 % of the halogenated material present.

Groundwater normally contains little organic matter or microbial contamination. Therefore, only small doses of active chlorine are needed for purification. Consequently total HBP levels are often less than 5 µg/l. Treatment of surface waters produces higher levels of by-products and even up to several hundred µg/l if the raw water is rich in organic matter. THM levels usually exceed HAA levels, generally by 50 – 300%, but if the raw water is from upland acid soils, for example, the situation can be reversed.

THM levels (and in the US also HAA levels) in drinking water are regulated and a variety of approaches is used to minimise HBPs in the drinking water. These include organic matter removal using filtration, coagulation, or activated carbon, etc; use of other oxidants for pre-treatment, focusing active chlorine use on final disinfection and residual chlorine; removal of by-products; pH at lower levels. The THMs evaporate, and the latter two gradually hydrolyse, thus reducing levels present in the water.

In **swimming pools**, pool operators maintain a residual amount of active chlorine to keep the water disinfected during use. In some countries a minimum level is set by law (typically 0.4 mg/l) and pH is also regulated close to neutral. HBPs are formed when organic matter in the water reacts with soils, sweat and urine introduced by swimmers. The main HBPs present in the pool water are THMs and HAAs, with chloral hydrate and dichloroacetonitrile at lower levels. The THMs evaporate, and the latter two gradually hydrolyse, thus reducing levels present in the water.

When hypochlorite solutions are used for **cleaning, bleaching or disinfecting** surfaces, fabrics or other items in homes, hospitals, the food industry and catering establishments the pH is again alkaline, or occasionally neutral. The range of HBPs formed is similar to those in drinking water and pools, but the range of organic matter is greater, so there is a greater proportion of unidentified substances.

Power stations and other industries abstract **cooling water** from rivers or the sea and organisms present must be controlled, for example to prevent them growing and 'fouling' (clogging up) the pipework, or spreading microbes which can be inhaled. The dosage of active chlorine used to chlorinate water for industrial purposes is about the same or a little higher than the amount typically in drinking water, so the range and levels of HBPs formed are similar. If seawater is used, most of the HBPs are brominated because the active chlorine creates active bromine by reacting with the bromide present.

When active chlorine is used for treating or disinfecting sewage the dosage is higher than for cooling water. Typically 10 – 40 mg/l is applied depending on whether chlorination is a pre-treatment or a final disinfection, and a residual of about 5 mg/l is maintained for one hour. THM and HAA levels may be a little higher than in drinking water, but because of the complex mix of organic matter in sewage, the range of unidentified by-products is inevitably greater.



Health effects

Adverse effects on health from HBPs (otherwise known as disinfection by-products) from the various uses of active chlorine depend on the hazards of the substances involved and the extent of exposure. Exposure to by-products is potentially greatest through drinking water, followed by using swimming pools. The suggested carcinogenic effects of HBPs have only been found in laboratory animals at levels many thousands of times greater than those found in drinking water. Evidence of harm to reproductive systems or developmental growth is sparse and the findings are inconsistent. Research has shown that chloroform (the main type of THM) is unlikely to cause cancer at low levels found in drinking water. The World Health Organisation concludes that the "risks to health are extremely small in comparison with inadequate disinfection". Drinking water disinfection in the EU is regulated by the 1998 Drinking Water Directive, which includes limits on HBPs. These will be further tightened in 2008.

In swimming pools, exposure to HBPs can be minimised by good hygiene and pool management. Human exposure to HBPs when active chlorine is used for cleaning and disinfecting, is far less than via drinking water. The use of 'active chlorine' in cooling and sewage treatment results in only minimal exposure for workers. No adverse health effects are thus to be expected.

Environmental effects

The former use of chlorine for bleaching paper pulp in Europe took place at acid pH in the presence of a wide range of phenolic and other easily-chlorinated substances, and under severe conditions. This produced a range of by-products including highly chlorinated, poorly biodegradable, bioaccumulative and toxic substances such as dioxins and furans. Chlorine dioxide or other oxidants, which do not give rise to these problems, are now used in Europe for bleaching paper pulp.

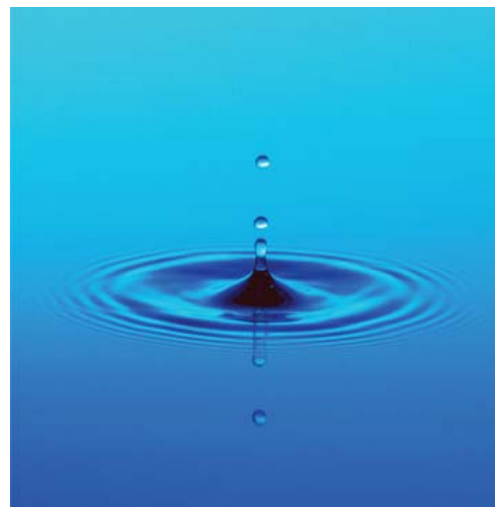
In contrast, the HBPs formed during cleaning and disinfection processes, which take place exclusively at neutral or alkaline pH, have been shown to be extensively biodegradable and water-soluble. They are effectively removed during sewage treatment and have little potential for bioaccumulation.

Detailed calculations for the major by-products, the THMs and HAAs, show that the levels entering the environment from all uses are well below² those at which any adverse effects might be expected.

For the unidentified HBPs the degree of chlorination is generally low, limited to mono- or di-chlorination in most cases. Much of the chlorination of organic matter is likely to be in the form of large molecules – sparsely chlorinated fragments of proteins for example – that will not exert toxic effects. Direct 'whole effluent' experiments representing various uses, including household laundry and sewage disinfection, have shown that no significant amounts of persistent, potentially bioaccumulative substances are formed. Toxicity tests on these mixtures containing HBPs show that the effluents do not increase the toxicity of sewage effluent.

The HBPs formed during cleaning and disinfection can be measured and are often referred to as Adsorbable Organic Halogen (AOX). However, this parameter gives no indication of potential for adverse environmental effects, because it does not discriminate between hazardous and non-hazardous substances. Most of the HBPs arising in current uses of active chlorine probably also occur naturally as a result of natural organic halogenation processes.

The total flows of halogenated by-products arising from use of active chlorine for microbial control and cleaning as described above do not seem likely to produce adverse environmental effects.



The chlorine industry in Europe

The European chlor-alkali sector produces more than 20 million tonnes per year of chlorine and caustic soda (as well as hydrogen). These products underpin 55% of European chemical industry turnover (2003: €580,000 million) and are used in a wide range of industrial and consumer applications.

The largest single application for chlorine is in the manufacture of PVC resin and for caustic soda it is the bleaching of pulp, paper and cellulose.

Producing chlorine

Chlorine is produced by electrolysis in enclosed cells using three different processes – mercury, membrane and diaphragm. Animated versions of these can be viewed on *Chlorine Online* at www.eurochlor.org.

Chlorination by-products is the first issue in Euro Chlor's new *Focus on Chlorine Science* series. The series aims to clarify and consolidate scientific research in the field of chlorine chemistry, facilitating the knowledge gathering of scientists, regulators and key decision makers. For further Euro Chlor science publications, visit www.eurochlor.org/science

Euro Chlor provides a focal point for the chlor-alkali industry's drive to achieve a sustainable future through economically and environmentally-sound manufacture and use of its products. Based in Brussels, at the heart of the European Union, the federation works with national, European and international authorities to ensure that legislation affecting the industry is workable, efficient and effective.