

Chemicals in Drinking Water: Chloramines

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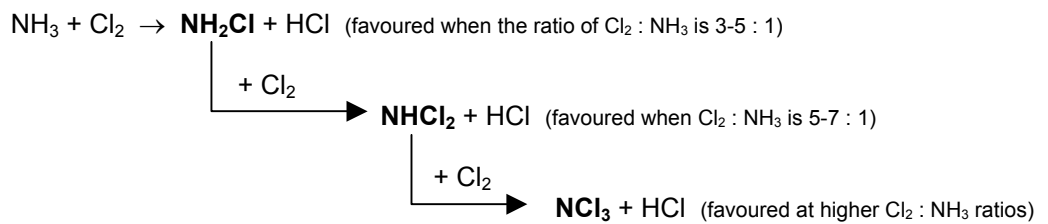
1 Background Information

Chemical names & formulae	Inorganic chloramines:	Monochloramine	NH_2Cl
		Dichloramine	NHCl_2
		Trichloramine (nitrogen trichloride)	NCl_3
	Organic chloramines:	R-NHCl where R=organic group e.g. CH_3 , C_2H_5	

Monochloramine should be recognised as being different from commercial products called *chloramine T*, *chloramine B* and *dichloramine T*. These products are sodium salts of chlorinated arylsulphonamides and are used as antibiotics or germicides in human medicine and as veterinary topical antiseptics and disinfectants. They are not approved for use in potable water supplies in the UK and are not formed as by-products in drinking or recreational water.

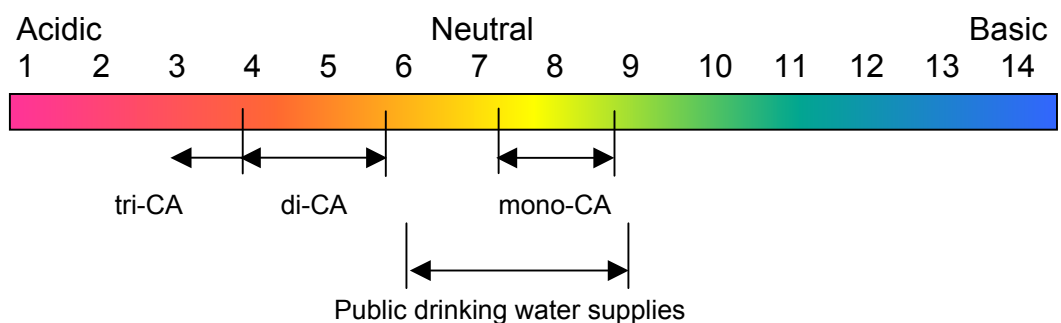
Description

Chloramines are products of the reaction between ammonia (NH_3) and chlorine (Cl_2). The chloramines speciation depends on the relative amounts of NH_3 and Cl_2 present:



pH ranges

Monochloramine is the first member of the homologous series and is the principal product formed at pH 7.5-9. However, higher chlorine concentrations in the water and lower pH results in the formation of di- and tri-chloramine.



Chloramines are formed as a result of the reaction between added chlorine and ammonia *naturally* present in the water or ammonia that has been deliberately added so that a combined chlorine residual will be formed.

Terminology

When results of water analysis refer to:

- **Combined** residual chlorine concentration, this denotes chlorine in the form of *chloramines*.
- **Free** residual chlorine concentration, this denotes chlorine in the form of *hypochlorous acid* (HOCl) and the *hypochlorite ion* (ClO⁻).

Uses

Monochloramine can be used as a **disinfectant** in water supplies and has the advantage of creating fewer by-products than when chlorine itself is used. Chlorination results in the formation of trihalomethanes (THMs) which are potentially hazardous and can cause taste and odour problems at high concentrations. Areas of the US, Canada and Britain have used monochloramine as a disinfectant for several decades and have demonstrated, in model distribution studies, it to be an effective inactivator of biofilm bacteria due to its greater penetrating power compared to free chlorine. Monochloramine is used as a disinfectant at concentrations that typically range from 1.5 to 2.5 mg / L.

The primary disadvantage of monochloramine is that it is a much weaker and slower acting disinfectant than *free* chlorine. It is particularly weak at inactivating certain viruses. In water systems that use monochloramine as a residual disinfectant, chlorine is usually used as a primary disinfectant so that microorganisms, including viruses, will be exposed to the free chlorine for a suitable period. Ammonia is then added at a point downstream from the initial chlorine application and the monochloramine is formed *in-situ* which then persists for longer period than free chlorine. A potential problem with the use of monochloramine is *nitrification*, caused by the action of ammonia-oxidising bacteria on excess ammonia from incorrect dosing.

Removal

Chloramines can be removed from water using activated carbon with low flow rates (5 to 10 minutes contact time), followed by residual ammonia adsorption using mineral zeolite media. The use of reducing agents such as sodium sulfite, sodium bisulfite, sodium thiosulfate and ascorbic acid (vitamin C) also removes monochloramine from water. Boiling and aeration are ineffective methods for monochloramine removal.

2 Exposure Routes & Standards

Drinking water

Chloramines are present both in chlorinated water and potentially as vapour above the surface of the water. Typical chloramine concentrations of 0.2–2 mg / L are found in drinking water supplies where monochloramine has been used as a primary disinfectant or to provide a chlorine residual in the distribution system. Whilst there is no UK standard for chloramines in water, the WHO recommend a maximum acceptable concentration for chloramines in drinking water of **3 mg / L** (rounded figure). This is based on a tolerable daily intake (TDI) of monochloramine of **94 µg / kg body weight** which itself is derived from a no observable

adverse effect level (NOAEL) of 9.4 mg / kg body weight divided by a safety factor of 100. The US EPA reconsidered the toxicity data for monochloramine when establishing a Maximum Residual Disinfectant Level Goal (MRDLG) and Maximum Residual Disinfectant Level (MRDL) for chloramines in drinking water which entered US legislation in 1998. The evaluation was based on the abovementioned NOAEL and determined the MRDLG and MRDL to be 4 mg / L (as Cl₂) equivalent to 3 mg / L monochloramine.

Household cleaning agents

Accidental mixing of solutions of ammonia and sodium hypochlorite bleach (NaOCl) results in the production of monochloramine and dichloramine fumes which are acrid and irritant.

Swimming pools

Chloramines are present in swimming pool water and in the atmosphere of the pool-hall as by-products from the reaction of ammonia (derived from the decomposition of urea and creatinine in nitrogenous human products e.g. urine and sweat) with chlorine-based disinfectants. The Pool Water Treatment Advisory Group recommend the concentration of free chlorine detectable (free chlorine residual) be kept as low as 1 mg / L and that the combined chlorine residual should be ideally half, or less, of that of free chlorine.

Concentration thresholds

Odour and taste thresholds for **monochloramine** of 0.65 and 0.48 mg / L respectively have been reported. The chloramines have a pungent odour. Dichloramine imparts a chlorinous odour to water, whereas monochloramine does not. However, complaints about drinking water supplies are not likely to result for concentrations below 3-5 mg / L.

Dichloramines may cause complaints at concentrations as low as 0.5 mg / L. However, problems with taste and odour are closely related to the ratio of mono- to di-chloramine and may result when the dichloramine concentration exceeds 20% of that of monochloramine.

Trichloramine, the most irritant, has a strong unpleasant odour at concentrations in water as low as 0.02 mg / L and, together with dichloramine, is largely responsible for the typical "indoor pool smell". The different volatilities of the chloramines result in substantial differences in the rates of release from water: di- and tri-chloramine are released ~3 and 300 times faster than monochloramine, respectively.

3 Metabolism & Toxicity Information

Human toxicology

It is likely that most of any ingested monochloramine would reach the stomach intact. However it decays rapidly in stomach acid and free monochloramine is not expected to enter the systemic circulation. Various types of transformation in saliva and gastric fluid have been suggested, including the formation of organic chloramino acids in gastric fluids. The precise nature of any metabolic products will depend on the pH, chloride ion concentration and organic substance concentrations. Short-term exposure of up to 24 mg / L of monochloramine in drinking water did not produce adverse effects. Volunteers given water containing up to 5 mg / L of monochloramine for 12 weeks also did not exhibit adverse effects.

No data are available on the toxicity of dichloramine or trichloramine in drinking water, however irritant properties are known to increase with chlorine content (toxicity: tri > di > mono). International guidelines for drinking water quality suggest that no short- or long-term health effects have been associated with chloramines in chlorinated drinking water.

To date, the International Agency for Research on Cancer (IARC) has not formally evaluated the carcinogenic potential of chloramines.

Animal toxicology Laboratory studies in rats suggest that monochloramine may be readily absorbed from the gastro-intestinal tract and is metabolised to the chloride ion, which is predominantly excreted in the urine. The carcinogenicity of monochloramine has been investigated recently by the US National Toxicology Program (NTP) who concluded that, under the conditions of the bioassay, there was *equivocal evidence* of carcinogenicity in female F344/N rats but *no evidence* of carcinogenicity in either male rats or B6C4F₁ mice of either sex. Although monochloramine has been found to be mutagenic in some *in vitro* animal studies, it has not been found to be genotoxic *in vivo* in mammalian cells.

Other chemical by-products from chloramination Chloramine does not usually produce chlorination by-products but in UK practice chlorine is usually dosed first followed by ammonia to make a chloramines residual. This produces a spectrum of disinfection by-products similar to that produced by ordinary chlorination but because the contact time is much shorter, lower concentrations of by-products (e.g THMs) tend to be produced than when free chlorine is used. Other by-products may be formed in very small amounts such as haloketones, chloropicrin, haloacetic acids, haloacetonitriles, aldehydes and chlorophenols. In contrast, two by-products are formed at *higher* concentrations following chloramination than chlorination: cyanogen chloride and, possibly, N-nitrosodimethylamine (NDMA). The possibility that other related N-nitroso compounds may also be favoured by chloramination is likely to receive increasing research attention.

4 Health Effect Information

Renal dialysis **The main potential problem relates to kidney dialysis patients:** Hospitals and kidney dialysis centres must therefore be alerted when chloramines are used for water supply disinfection. Cases of chloramine-induced acute **haemolytic anaemia** and **methaemoglobinaemia** have been reported in patients when their dialysis water was not appropriately treated to remove chloramines. Patients subsequently required transfusion to treat the resultant haemolytic anaemia.

In the dialysis process, water comes in contact with the blood across a permeable membrane. Most membranes will not remove chlorine or chloramines. In fact, both chlorine and chloramines are damaging to most (but not all) membranes. They should therefore normally be removed prior to processing water through reverse osmosis membrane systems. Chloramines remaining in water would be harmful, just as chlorine is harmful and must be removed prior to use in kidney dialysis machines. There are two ways to do this: either by adding ascorbic acid or by using a granular-activated carbon treatment.

Everyone (including kidney dialysis patients) can **drink, cook, and bathe** in chloraminated water.

The following methods are **not effective** for removal of chloramines: boiling, distillation, letting water stand for a day or two, reverse osmosis, and reagents for removing only free chlorine.

Drinking water

As already mentioned, international guidelines for drinking water quality suggest that no short- or long-term health effects have been associated with chloramines in chlorinated drinking water. Chloramines are therefore considered as safe water treatment chemicals when present at the normal concentrations detailed above.

Household cleaning agents

Inhalation of the chloramine fumes results in burning in the eyes and throat, transient cough, dyspnoea, nausea and vomiting. In mucosa, chloramines decompose to ammonia (NH_3) and hypochlorous acid (HOCl), which can then dissociate to hydrochloric acid (HCl) and nascent oxygen (O). Corrosive effects of ammonia and hydrochloric acid also contribute to chloramines-induced respiratory tract damage. Metabolic acidosis also is a rare complication of serious poisoning.

Swimming pools

Chloramines in and above swimming pool water are known to cause irritation of the conjunctiva and the mucous membranes of the nasopharynx, and may precipitate acute asthma.

Monochloramine is stable at normal pool pH values and is not an irritating compound.

Dichloramine irritates the eyes and nose.

Trichloramine is the most irritant, affecting the eyes, nose, throat and respiratory tract.

Lifeguards, due to their prolonged exposure to trichloramine from indoor pools, may be at risk of developing irritant eye, nasal and throat symptoms. The possibility that these individuals may develop transient bronchial hyperresponsiveness cannot be excluded. It is therefore important that appropriate steps are taken to manage swimming pools to minimise the formation of chloramines.

5 Sources of Information & Acknowledgements

WHO World Health Organisation "Guidelines for drinking-water quality", Vol. 2, 1996, Chapter 16: Disinfectants & disinfectant by-products.
www.who.int/water_sanitation_health/GDWQ/Chemicals/chloraminefull.htm

Health Canada "Chloramines" Guidance Document, October 1995
http://www.hc-sc.gc.ca/ehp/ehd/catalogue/bch_pubs/dwgsup_doc/chlora.pdf

OHM / TADS Oil & Hazardous Materials / Technical Assistance Data System
Chloramines datasheet

PHLS Public Health Laboratory Service
"Factors associated with seeking emergency treatment following suspected chemical contamination of a leisure pool", *Comm. Dis. Pub. Health* **2000**, 3, 208-211.
www.phls.co.uk/publications/CDPHvol3/No3/chemical.pdf

WQA Water Quality Association
"Chloramine – Are there negative health effects?"
www.wqa.org/site/ologic.cfm?ID=348

Prepared by: Dr Steve Hankin
Epidemiologist – Chemical Incidents
Scottish Centre for Infection & Environmental Health
Clifton House, Clifton Place
Glasgow G3 7LN

Tel: (0141) 300 1117 Fax: (0141) 300 1170
Email: steve.hankin@scieh.csa.scot.nhs.uk
Website: www.show.scot.nhs.uk/scieh/

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