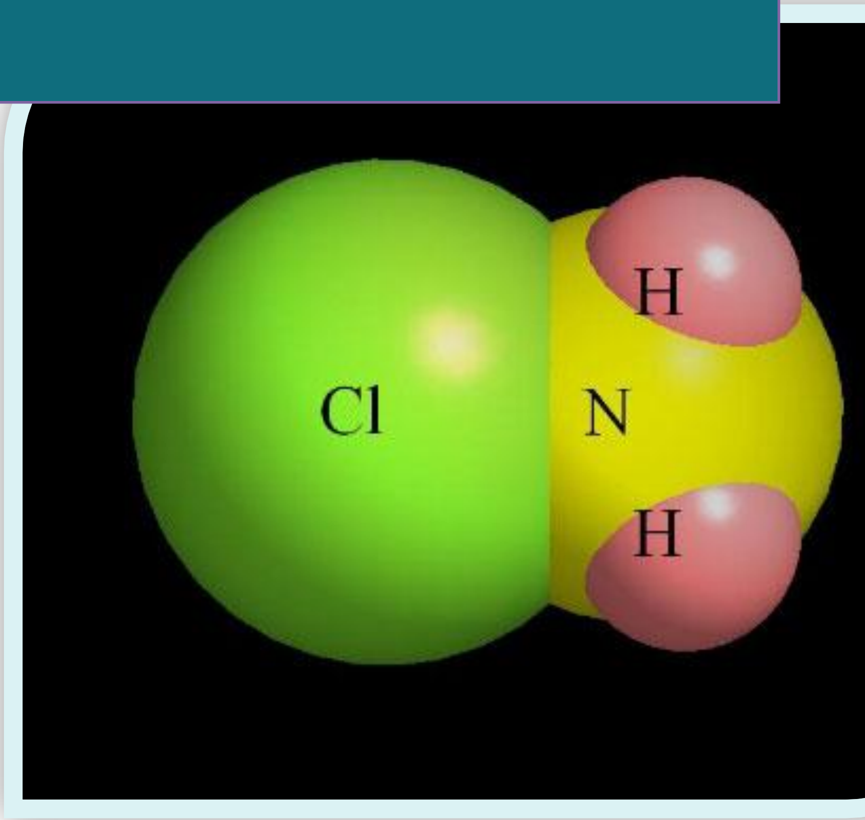
Literature review on the effects of switching monochloramine for chlorine in disinfection



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Contents

1.0 Introduction

This work was commissioned under the CREW call down service. The object of the project was to carry out a literature search on the effects of switching from chlorine to monochloramine for water disinfection, specifically with regards to the effects on lead and copper corrosion. Information was sought on current understanding of disinfectant choice on lead and copper corrosion; the lessons learned from a Washington case study, and guidance on the appropriate sampling protocol for lead and copper measurements.

2.0 Background

The water industry is required to deal with complex chemistry and at the same time meet ever more stringent quality standards. Sometimes, as a result of chasing one particular standard, changes to the water chemistry have affected the quality of the water in unforeseen ways. For example, the pH adjustment of water, to reduce lead and copper corrosion, in conjunction with the use of free chlorine disinfectant has been found to increase the production of disinfection by-products (DBPs), such as trihalomethanes[1]. These products of free chlorine and natural organic matter, have been recognised as carcinogenic, neurotoxic and tertogenic.[2]. The EU Drinking Water Directive (98/83/EC) put an overall limit on total trihalomethanes of 100 $\mu g.l^{-1}$, but the World Health Organisation, in 2005, suggested guidelines for drinking water quality that put limits on individual compounds[3].

To reduce the production of known DBPs, water authorities around the world have begun to switch to disinfection using monochloramine, which is formed by mixing chlorine and ammonia during the disinfection process. In 2004, it became clear that this switch could lead to unintended consequences, when serious overshoots non-compliance of acceptable lead levels in drinking water were found across Washington DC.

3.0 Washington discovery and aftermath

The Washington Water and Sewer Authority (WASA) replaced chlorine with chloramine disinfectant in November 2000[4, 5]. Although a rise in the level of lead in water was detected in 2002[6], it was below the action level and further increases were not anticipated. In 2004, 18% of Washington homes had lead service lines[7].

The first indications of serious problems were seen by an academic asked to investigate problems with pinhole corrosion in copper pipes in 2003[4]. As part of his checks he also measured lead levels and found them to be very high. He was then contracted by the US EPA and WASA to investigate the problem further, but during the work came under pressure to restrict access to the data. The lead problem eventually was made public in 2004 after an investigation by a Washington Post reporter[8]. Although it was clear that high lead levels were being found, WASA were initially unwilling to disclose the results of their surveys. Further public disclosures suggested that a cover-up was being attempted (although this was probably more due to panic than a deliberate attempt to mislead), and WASA was forced to accept the problem and take action.

WASA began adding orthophosphate as a corrosion inhibiter in July 2004, and also started a programme of replacing lead service lines leading to properties. However, replacement of the lines from the street and of plumbing within buildings was the responsibility of the owners and cost issues meant that, in many cases, only partial replacement of the lead piping was achieved[9]. The replacement programme was stopped in 2008, partly because there were indications that partial replacement was leading to higher lead levels in the water[10].

A lead screening programme, involving 6,835 Washington residents was implemented between February and July 2004. It was found that only 65 of 2,342 children between 6 months and 6 years of age had blood lead levels (BLL) higher than 10 $\mu g\ dl^{-1}$ [6]. Another study has reviewed blood lead levels in Washington children for the period 1998-2006[9]. The study found that lead service lines were a risk factor for BLL in children, even when the measured lead levels in water were below the EPA action level. Use of chloramine alone produced higher BLL than when chlorine alone or chloramine with orthophosphate was used. Another recent analysis of data[11] found that the incidence of BLL of more than 10 $\mu g\ dl^{-1}$ in young children (less than 16 months) was four times higher in the period 2001-2003 than it was in 2000, before the substitution of chloramine.

The detrimental impact of chloramine substitution on water lead levels has also been seen in other parts of the USA. Data from Wayne County, North Carolina indicated that the addition of chloramine to drinking water may increase BLL in children[2]. Chloramine use was also linked to higher BLL in children in Greenville, North Carolina[12].

4.0 Mechanisms of corrosion enhancement as a result of chloramine use

It is believed that free chlorine promotes the formation of PbO_2, a relatively insoluble Pb (IV) oxide. Replacing the chlorine with chloramine eventually reduces the oxides to Pb (II) compounds[13-15], which are much more soluble[16] or porous[17], allowing lead to leach into the water.

The standard method of dealing with this enhanced corrosion effect, adding orthophosphate to the water as a corrosion inhibitor, reduces but does not eliminate the increase in the children's BLL when chloramine is present[9]. A recent paper also suggests that, while orthophosphate lowers the level of soluble lead, it may lead to an increase in the formation of particulate lead[14].

There is also evidence of interactions of chloramines with other additives such as coagulants and fluoridation agents that may produce compounds that disrupt the lead oxide scales formed on old lead piping[2]. The chloride to sulphate mass ratio (which is affected by the coagulant used in treatment) in water has also been shown to have a major effect on lead corrosion [18, 19]. Fluoridated waters also exhibit higher lead levels than those without fluoridation[20], although fluoridation usually corresponds with chloramine use and it isn't clear what their relative effects are. A study on lead leaching from leaded-brass [21] has indicated that there is a synergistic effect between chlorine or chloramines, and fluoridation agents.

Partial replacement of lead service lines is common, where water authorities are only responsible for piping in the street, and feed lines and internal plumbing are the responsibility of the owner. There is evidence that partial replacement could cause galvanic effects that enhance lead release[22]. Plastic couplings between the lead and copper lines can eliminate this effect. A recent study [9] detected no significant differences in the BLL in children in properties with full lead service lines, and those where the lead had been partially replaced. In both cases, however, the BLL were significantly higher than those where no lead was present in the piping. The study was carried out from data from Washington when both chloramine and orthophosphate was being added to the water.

Another possible corrosion mechanism involving the decay products of chloramine has been suggested [23].The chloramine is assumed to decay first to chlorine and ammonia, and then the ammonia is converted, by biological action, to nitrite and then nitrate. Simulated tests indicate that this could significantly enhance corrosion in lead solder. Ammonia from chloramines has also been implicated in the corrosion of brass fittings containing lead [5].

5.0 Problems with sampling to estimate lead exposure

There is no universally accepted method of sampling for lead in drinking water. The Drinking Water Directives indicate that water should be sampled at the consumers tap, and done so in such a way as to be representative of the weekly average ingested by consumers. It does not, however describe how this should be achieved [24]. The USA has a more proscriptive regime with a specified number of fixed monitoring points (based on population) and action limits on the levels that are observed.

Lead levels in water are dependent on the many factors that can affect solubility, such as pH, temperature and the concentration of various substances such as carbonates, orthophosphate, chlorine and silicate. In addition, the lead levels in water systems are affected by physical factors such as time, pipe arrangements and flow-rates. It appears that the concentration of lead recorded at a particular site tends to be subject to frequent repeated 'spikes'[25].

Computational modelling has been suggested [24] as a way of investigating the variability of results from lead sampling. The models were used to compare the likely results for a range of different sampling regimes (daily average concentrations (DAC), random daytime sampling (RDT), 30 minute stagnation sampling (30MS), and 6-hour stagnation sampling (6HS)). It was found that: RDT and DAC would produce similar results for waters with moderate plumbosolvency; RDT is more stringent than DAC for low plumbosolvency; that all random sampling methods have poor reproducibility; and that stagnation sampling from a fixed point may not be representative. The comparisons however suffer due to the exclusion of particulate lead. Other work [26] has suggested that particulate lead is the primary contributor to total lead in flowing systems, although it is only significant in stagnated systems at higher water pH values. Another study, which measured lead levels in homes where high BLLs had been detected in children, found that particulate lead could account for up to 80% of the total lead in a water sample [27].

Current sampling techniques and methods of analysis may underestimate total lead because of the particulate component [28]. RDT may be a better method than 30MS of estimating particulate lead at the tap, as 30MS sampling involves a 5 minute flushing prior to stagnation, which is likely to remove most of the lead particles.

The problem of particulate lead seems to be greater in partially replaced lead service lines, where galvanic corrosion increases the rate of formation of particulates [29]. The particulates produced cause spikes in measured lead levels at high flow-rates.

6.0 Effect of chloramines on copper corrosion

It is known that free chlorine, chloramines and free ammonia all increase the corrosion of copper[30]. The effects of free chlorine are strongest in new pipes, which lack protective oxide layers. The effects of free chlorine are also highly dependent on pH and on other materials that may be present in the water such as chlorides, sulphates and natural organic materials [1]. However, free ammonia and ammonia resulting from chloramine breakdown may have the potential to disrupt established oxide layers in older copper pipes, leading to increased corrosion rates, although more work needs to be done to establish if this is, in fact, the case.

7.0 Other potential problems from the use of chloramines

Chloramine is effective against most water pathogens, but is ineffective against *cryptosporidium* [31]. Free chlorine needs to be used in addition to chloramine, often as a pre-treatment prior to ammonia addition but sometimes periodic flushing of distribution systems with chlorinated water may be required.

Decomposition of chloramines, or incorrect dosing of ammonia, can result in free ammonia in the water and thus to nitrification. Nitrification causes a range of potential problems: increased corrosion [23]; dissolved oxygen depletion; reduction of pH; and increases in ammonia and nitrite oxidising bacteria[32].

In addition to increasing lead and copper corrosion it is now clear that chloramines can cause the decay of other materials commonly used in plumbing systems like plastics and rubber. Chloramine exposure is significantly more destructive to elastomers than free chlorine, and a larger number of failures of elastomer components have been noticed in the USA after switching to chloramine. The largest number of complaints were related to toilet tank components (tank balls, flapper valves, glands and diaphragms) which were failing after six months, rather than the expected service life of at least five to six years[33].

Most worryingly, given that chloramines are being used to reduce dangerous DBPs**,** it has been reported [34] that chloramines can react with common precursors to form a different set of harmful DBPs. In particular, carcinogenic nitrosamines are produced when chloramines react with nitrogen containing organic materials, such as the synthetic polymers used for water softening and flocculation [35, 36].

8.0 Recommendations from the literature

One option is to use chloramines for disinfection, but then to use other materials to inhibit the corrosion processes. However, controlling water chemistry by the addition of corrosion inhibitors such as orthophosphate may only be partially successful. Some water authorities, such as the San Francisco Public Utilities Commission, have reported complete success in using high pH (8.6 to 9.4) to minimise the release of lead and copper, such that the switch from free chlorine to chloramine had no effect on lead levels[37]. Although this is against a background of complete replacement of lead service lines in the 1980s and the minimisation of other lead containing components in water mains. Others, such as Providence Rhode Island in the USA, have been unable to reduce lead below trigger levels by water chemistry and are now engaged in a programme of replacing lead piping [38]. The cost of orthophosphate dosing is also significant, and at least one water authority in the U.S. (Madison Water Utility) decided that full lead service line replacement was cheaper[10].

Given the known problems of enhanced lead and copper corrosion and the potential formation of hazardous DBPs caused by the use of chloramines, it has been suggested that a switch away from chlorine may not be advisable [34, 39]. Instead it may be better to continue chlorination, but remove the DBP precursors first. However, at the moment it is unclear how this could be achieved and more research is required. Current research on-going at the James Hutton Institute and elsewhere is comparing compositional quality of natural organic matter (using spectroscopic methods) in waters with their respective trihalomethane production potentials following chlorination. This will ascertain which water chemistries have the highest risk of total trihalomethane production and chemical interactions that produce these DBPs.

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