



INNOVATING WATER HYGIENE

Monochloramine: the Science Behind

The reasons why monochloramine
is the most effective and non corrosive
disinfectant against *Legionella*

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Executive Summary

Legionella & the problem of the correct disinfectant

Legionellae are ubiquitous bacteria with a worldwide spread in natural and artificial water environments, able to survive in a range of environmental conditions. Their ability to colonize our artificial water systems represents a serious concern for public health, since they can cause pneumonia and other respiratory illness (collectively referred to as “legionellosis”), especially in susceptible individuals.

Nowadays, several strategies are available to fight against *Legionella* and attain water disinfection, but most of them, while having an appreciable disinfectant power, can also be responsible for significant side effects, both on water system conditions, frequently causing corrosion issues, and on human health, due to the potential generation of toxic disinfection by-products.

This document will provide the readers with evidences from the international scientific literature that demonstrate why monochloramine is the best solution to effectively solve the problem of *legionella* contamination in building water systems and to optimize the disinfection process.

What is Monochloramine?

Section 1 describes monochloramine chemical properties, the secret of its effectiveness. It is a chlorine-based disinfectant, synthesized from hypochlorous acid and an ammonium salt in a reaction that it is particularly favoured at the pH values typical of drinking water.

Thanks to the nature of the chemical bonds in the molecule, monochloramine is a mild oxidant and a stable substance (especially if compared with other chlorine-based disinfectants, as hypochlorous acid-hypochlorite and chlorine dioxide): these features enable it to effectively reach and kill bacteria by penetrating the biofilm (the slimy matrix produced and inhabited by bacteria cells) and to maintain its effectiveness and proper concentration even in low flow regimes and at distal points of complex building water systems.

Section 1 also explains why the use of properly produced monochloramine can help in minimizing the generation of regulated disinfection by-products like THMs, chlorite and chlorate, haloacetic acids and chlorinated organic molecules. Finally, the volatility issue is taken into account: monochloramine volatility has proven to be negligible and does not affect its efficacy.

The correct strategy to disinfection

Section 2 offers some remarks about the driving forces to take into account in defining the most suitable strategy for water disinfection in building water systems, to ensure a consistent disinfectant residual in the building pipes. The choice of dosing the disinfectant either on the main cold water line or on the domestic hot water loop it is a crucial issue. The factors guiding this choice are related to the chemistry, the microbiology and the economics.

Despite it is impossible to define an universally applicable disinfection approach, in general it should be considered that:

- The addition of the disinfectant directly in the hot water system avoids the “thermal shock” that can contribute to increase the disinfectant decay ratio (however limited for monochloramine) and subsequently helps in ensuring a better dosage control and in reducing by-product formation (chemistry).
- Due to the optimal temperature growth conditions, *Legionella* colonizes primarily in hot water, therefore treating all the cold water system would be useless in most of the cases (microbiology).
- Treating the all the incoming cold water of a building results in high equipment and operational costs since bigger disinfection units have to be installed and bigger volume of reagents are going to be consumed (economics).

If properly produced, monochloramine is not involved in nitrosamine generation process

Section 3 is focused on one of the main emerging concerns related to the use of monochloramine for water disinfection: the formation of nitrosamines. Different studies are reported confirming that, if properly produced, monochloramine is not involved in nitrosamine generation processes. When monochloramine is produced according to specific requirements in terms of chemical parameters, it is possible to avoid dichloramines formation, that can in turn contribute to nitrosamines generation.

Why there is no corrosion problem

Section 4 address the corrosion issue, that is a serious drawback of the application of oxidizing chemicals for water disinfection.

Being strong oxidants, the other chlorine-based disinfectants (chlorine dioxide in particular), are extremely aggressive toward both metallic and plastic pipes, causing premature ageing phenomena and pipes failures. Being a milder oxidant, monochloramine is perfectly compatible with all the pipe materials commonly used into building water systems.

Regulation

The main information about the European regulation and US regulation are explained in Section 5. In the European legislation, a biocide is defined as a chemical substance intended to destroy, deter, render harmless, or exert a controlling effect on any harmful organism. In order to harmonise the market at Union level, the EU issued the Biocidal Products Regulation (BPR, Regulation (EU) 528/2012).

According to Art. 95 of the BPR, as of September 1st 2015, a biocidal product consisting of, containing, or generating a relevant substance, cannot be made available on the EU market unless the substance supplier or product supplier is included in the list for the product type(s) to which the product belongs.

Sanipur submitted its own Biocide Dossier for monochloramine to ECHA respecting the deadline of Sept. 1st 2016. Thus, nowadays, Sanipur - founding partner of the “European Monochloramine Cooperation” - is one of the only two European companies (and the only one in Italy) listed on the “Art. 95 list” for the use of monochloramine for drinking water disinfection (BPR - PT5).

Sanipur is also the only company who has all its monochloramine generators models certified NSF/ANSI/CAN Standard 61 in the USA and Canada market.

NSF/ANSI/CAN Standard 61 was developed to establish stringent requirements for the control of potential adverse human health effects from products that contact drinking water, as supplemental water disinfection units.

Certification to NSF/ANSI/CAN Standard 61 ensures that the SANIKILL monochloramine generators meet the regulatory requirements for the U.S. and Canada,

Disclaimer

The authors are affiliated to Sanipur S.r.l. Headquarter (Italy) and Sanipur US LLC, which distribute and provide disinfection technologies based on chlorine, chlorine dioxide and monochloramine for *Legionella* remediation. This White Paper is a scientific report based on peer reviewed references that, in its purpose, would like to be unbiased by the commercial activity of Sanipur.

1

The Iron Fist in the Velvet Glove

1.1 Understanding chlorine-based disinfectants chemistry: the beauty of the electron clouds

US-EPA listed disinfectants for drinking water are all based on the Cl atom¹. The efficacy of these disinfectants vary significantly according to their chemical properties, as shown in the picture below:

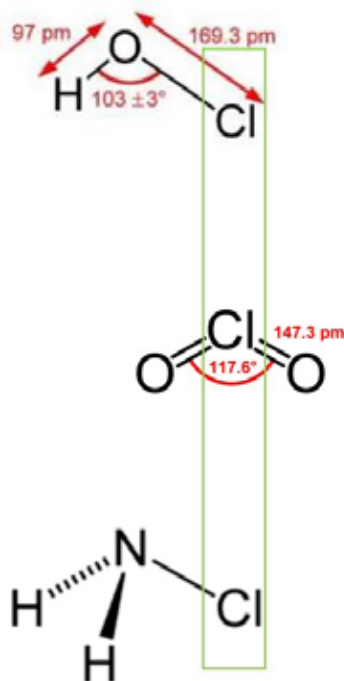


Figure 1: EPA listed disinfectants for drinking water

Chlorine (Hypochlorous acid hypochlorite) is the less effective among Cl-based disinfectants and at least 2-3 ppm are needed to reach a fair remediation. Under these conditions chlorine is highly corrosive against both metallic and plastic piping. Its effect is strongly pH-dependent and regulated toxic by-products (Trihalomethanes - THMs) may form.

Chlorine dioxide is a very effective disinfectant and 0.3 – 0.5 mg/l levels are enough to provide a good remediation but under these conditions chlorine dioxide is very aggressive on all piping materials and as a gas in solution is difficult to maintain residuals in hot water.

Monochloramine is the most effective Cl-based disinfectant and it is also the most materials respectful. It is effective at concentration of 2-3 mg/l, that can attain a 0% colonization within a few weeks of continuous application. Thanks to its stability, it is very effective in complex building plumbing system.

As suggested by the chemical formulas reported in Figure 1, hypochlorous acid (the dissolved form of chlorine) and monochloramine have a similar chemical structure while chlorine dioxide is completely different. This is because the Cl atom has the same oxidation state in the first two molecules. Meaning: chlorine/hypochlorous acid and monochloramine are “sister molecules”.

But why is the first an acid while the second acts more like a base? This is because of the different behavior of their partner atoms. Figure 2 shows the electron densities (Van der Waals surfaces) around the two molecules. Oxygen is considered a hard atom, it keeps much of the electron density close to itself (reddish cloud) and this gives rise to a strong oxidizers: chlorine, depleted of electrons, tends to break the bond with oxygen looking for an electron-donor partner.

Nitrogen is a soft atom (the red cloud is spreaded all over the bond between Cl and N) and the

¹ <http://water.epa.gov/drink/contaminants/basicinformation/disinfectants.cfm>

molecule it generates – monochloramine, NH_2Cl – is less oxidant compared to those with oxygen: chlorine is less prone to break the bond with nitrogen since this atom tends to share its electrons with the partner atoms. This is the main reason for the different chemical behavior of these molecules.

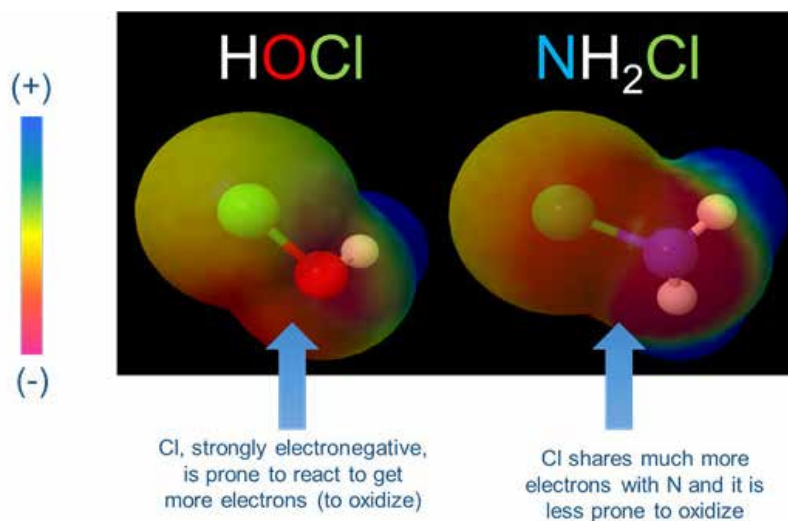
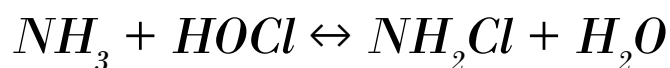


Figure 2: Van der Waals surfaces (representing electron density) of HOCl and NH_2Cl . Modeling and calculations are made by the author with MolView v2.1.3

In a nutshell, monochloramine is a “chlorine species” that masks its oxidizing power with a softer partner-atom (nitrogen instead of oxygen): like *an iron fist in a velvet glove*.

In fact, monochloramine is synthesized from hypochlorous acid and ammonia or an ammonium salt (usually chloride or sulfate) as follows:



Reaction 1: Monochloramine generation from ammonia and hypochlorous acid

As suggested by the electrons densities depicted in Figure 2, chlorine abandons oxygen for a new electron-donor partner.

During this reaction, other chloramines can form (di and tri chloramines, respectively NHCl_2 and NCl_3) and pH plays a key role in the selection of the desired product.

The following picture (Figure 3) shows the effect of pH on the relative concentration of these three molecules:

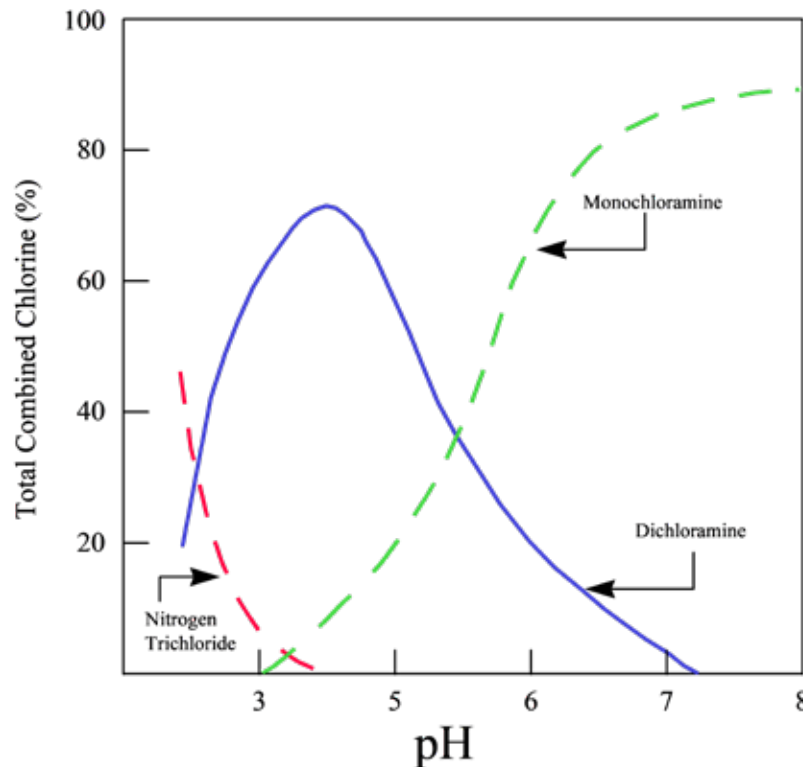


Figure 3: chloramines species as a function of pH. Source: Palin, A. 1950. "A Study of the Chloro Derivatives of Ammonia." Water and Water Engineering. 54:248-258

Monochloramine is very stable and the predominant species at pH above 7.2. At these pH values dichloramine and trichloramine (indicated as nitrogen trichloride) cannot form. During chloramination it is important to avoid the formation of di and tri chloramines since they are odorous and toxic molecules. Moreover trichloramine is an explosive liquid, but fortunately it cannot form in the normal drinking water matrix.

The following picture (Figure 4) shows the forms in which chlorine can be present at different pH. Hypochlorous acid, the actual biocide, is the predominant form in the pH range 3 to 7. At higher pH it dissociates to hypochlorite ion, which, despite remaining a strong oxidizer, is a weaker biocide.



Reaction 2: Hypochlorous acid dissociation

The comparison between the Figures 3 and 4 clearly shows that in the pH range of drinking water monochloramine is present 100% in its active form while hypochlorous acid is present

in a mixture with hypochlorite ion and that the percentage of the active form of free chlorine

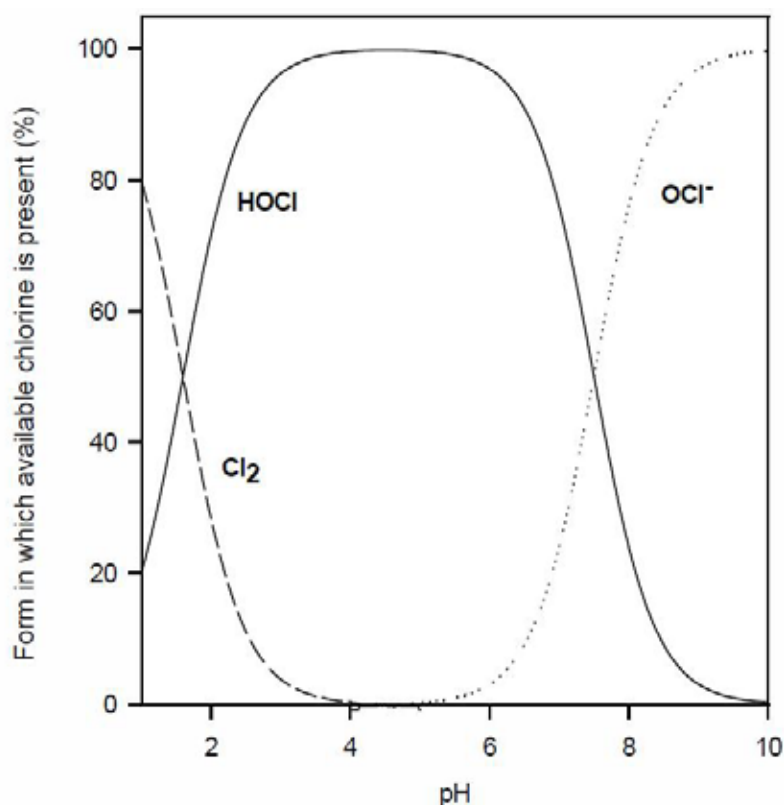


Figure 4: different free chlorine species present as a function of pH

declines sharply as the pH increases.

This is an important feature showing that free chlorine loses its biocide activity (less HOCl) as the pH increases while it keeps its oxidizing power (OCl⁻ being a strong oxidizer). This explains the high corrosive potential of free chlorine in drinking water treatment, where pH as high as 9.5 can be achieved (see Figure 5). At a pH of 8.0, the common pH for recirculating domestic hot water system, 80% of chlorine feed is hypochlorite leading to lower biocidal efficacy and much higher corrosivity. By contrast, a pH of 8.0 is ideal for the formation of monochloramine leading to high biocidal efficacy and much lower corrosivity. Working namely as an “iron fist in a velvet glove.”

Monochloramine, a weaker oxidant and a weaker biocide, does not show any appreciable difference in its activity in the drinking water pH range.

It is essential to consider the pH effect described above while comparing the efficiency of different disinfectants: in the case of chlorine, a high fraction of the chemical added to the water is in a form having no antimicrobial activity but a strong oxidizing corrosive effect. Moreover, such a fraction gradually and significantly increases with the increase of the pH value.

For example, in order to have 1 ppm of active free chlorine (HClO) at pH 8.0, it is necessary to

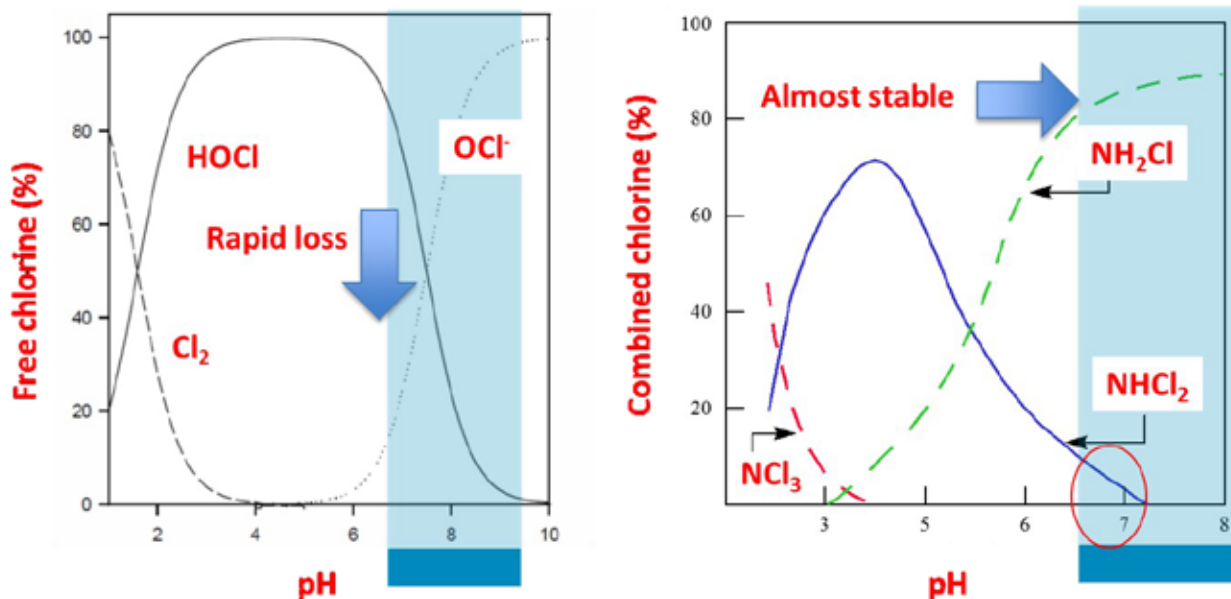


Figure 5: comparison of the graphs in Figure 3 and Figure 4 showing the different concentration of the active biocide (chlorine or chloramine) in the drinking water pH range (blue strips)

add 5 ppm of chlorine, since 80% of it dissociates into inactive hypochlorite ions (OCl^-). Whereas, in order to have 1 ppm of monochloramine, the addition of only 1 ppm is required: no wasted chemicals, no corrosion issue, less by-products.

Chlorine dioxide behaves differently from the other two Cl-based biocides, chlorine and monochloramine.



Reaction 3: resonance structures of chlorine dioxide

Its chemistry is very complex and fascinating. First of all, it is a radical, having an unpaired electron (as represented by the dotted red lines in Reaction 3), thus it is very reactive. Its reactivity is not significantly influenced by pH in the drinking water pH range. Its reactive nature is responsible for its typical low CT values² as a disinfectant, but also for its high corrosivity. Its corrosivity is enhanced by the fact that it is a dissolved gas and not a molecule in solution: this allows it to penetrate the crystalline structure of plastic pipe and break bonds in stabilizer molecules and polymer chains. The pipe becomes brittle and cracks appear on the inner surface. When the cracks become bigger the pipe starts leaking. This will be discussed further in a dedicated section of this paper.

The comparison of the CT values of the different disinfectants shows that monochloramine has

higher CT than chlorine and chlorine dioxide. This is due to the previously described lower oxidation potential of this disinfectant. This is not a drawback, however, since the stability and low reactivity of monochloramine helps it to better penetrate biofilms and kill bacteria inside it. This is why *monochloramine is the best biocide for secondary disinfection* (especially in domestic hot water loops) where long contact time between the biocide and the bacteria is achieved. *This feature is particularly useful to avoid contamination in dead legs during commissioning and renovation.* Low reactivity and stability help monochloramine to be effective and maintain proper concentrations even in low flow regimes (oversized pipes, temporary dead legs, varying flow situations) where other biocides will fail.

The following paragraphs review the impressive results in the investigation of the efficacy of monochloramine reported in the scientific literature.

² CT is a measure of the disinfection process reaction time and it is defined as the product of the disinfectant concentration (expressed in mg/L) and the time (in minutes) that potential pathogens in water are in contact with the disinfectant. CT values are assigned for various microorganisms and are specific for a given temperature and pH of the water. [Definition from Laura J. Rose et al., Appl. Environ. Microbiol., 2007; 73:3437–3439].

1.2 Biofilm penetration: monochloramine does it better

Biofilms are aggregates of microbial cells, usually accumulated at a solid-liquid interface and encased in a matrix of highly hydrated extracellular polymeric substances (EPS). The EPS structure not only promotes the binding of organic and inorganic compounds, enhancing the localized availability of nutrients, but also offers a protective environment against disinfectant residuals, creating a sort of protective barrier.

Monochloramine stability and low reactivity are the reason why it penetrates biofilm. This is a key feature of its disinfection properties.

The following picture shows the different penetration profiles into the biofilm for chlorine/hypochlorous acid and monochloramine, as previously reported in the scientific literature (Lee et al., 2011).

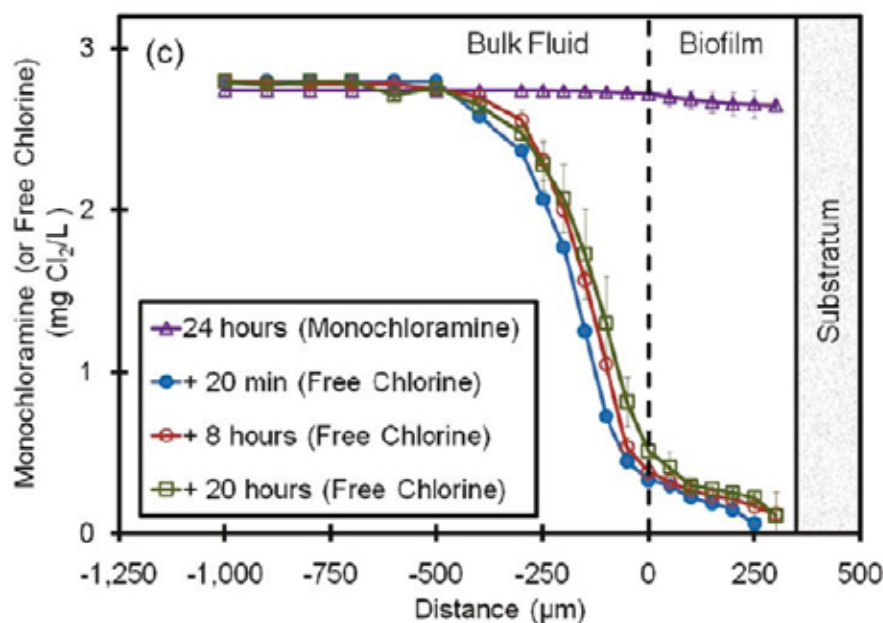


Figure 6: biofilm penetration of free chlorine and monochloramine determined by microelectrodes (Lee 2011).

Monochloramine and free chlorine have similar diffusion rates in water at 77°F (25°C), so they can reach the biofilm with similar kinetics. When they reach the biofilm, they can either react with the biological material of EPS excreted by microorganisms, being thus consumed, or they can continue the diffusion process, reaching the inner layers where bacteria are located. The measured free chlorine microprofiles shown in the picture detail the different behaviors between free chlorine and monochloramine with biofilm constituents. Whereas chlorine promptly reacts with EPS and is therefore consumed, monochloramine diffuses in the biofilm without being consumed. Free chlorine reacts faster with EPS and the external biofilm layers and it is consu-

med before reaching the inner regions of the biofilm where most of the *Legionella* bacteria lurk. *This is the first published demonstration of the superior ability of monochloramine to penetrate biofilms.* There is only one publication (Jang et al., 2006) dealing with chlorine dioxide biofilm penetration that the author was able to find in the scientific literature. It deals with biofilm penetration of chlorine dioxide in dairy equipment disinfection. Despite the concentrations tested are higher than those typically encountered in drinking water application (0.2 – 0.8 mg/l), it is impressive to note that the penetration profile of this molecule is similar to that of chlorine.

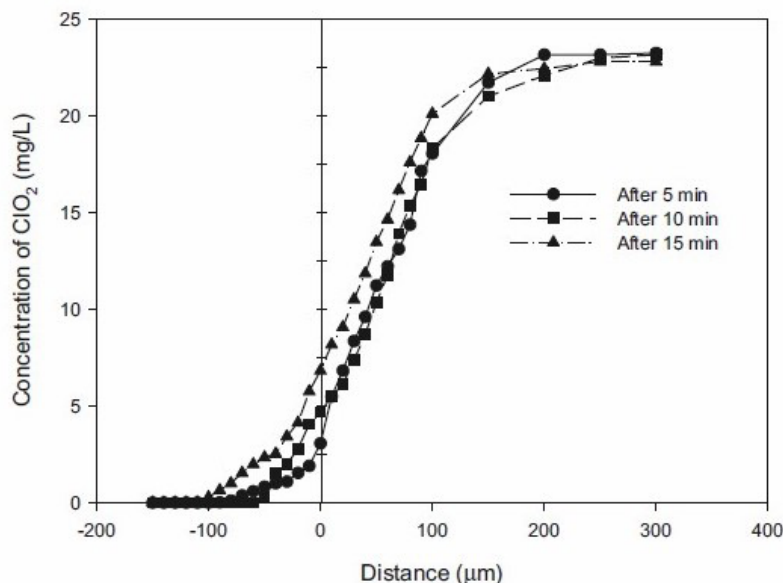


Figure 7: biofilm penetration of free chlorine dioxide determined by microelectrodes (Jang 2006).

Diffusion coefficients calculated in water for chlorine, chlorine dioxide and monochloramine are very similar (Cl_2 $1.66 \times 10^{-5} \text{cm}^2/\text{s}$, ClO_2 $1.35 \times 10^{-5} \text{cm}^2/\text{s}$, NH_2Cl $1.44 \times 10^{-5} \text{cm}^2/\text{s}$; from Jang et al., 2006 and Lee et al., 2011), thus the differences in biofilm penetration are substantially due to the different reactivity of these molecules: having reaction rates higher than diffusion rate, chlorine and chlorine dioxide do not effectively penetrate the biofilm as monochloramine does.

It is important to note that such a higher biofilm penetration means no waste of chemicals: to achieve the same biofilm penetration chlorine or chlorine dioxide must be added in higher concentration, since they are largely consumed reacting with the external biofilm layers. Dosing higher amount of chemical (much of it wasted) means higher costs of treatment and compliance issues with drinking water regulatory agencies. In the case of chlorine, at the usual drinking water pH only a fraction of chlorine is active free chlorine, the remaining part is not only a waste, but also a strong oxidizer (hypochlorite ion) added to the water. This strong oxidizer is responsible for the high metal corrosion rate of the chlorinated water compared to the chloraminated water.

1.3 Efficacy of monochloramine for *Legionella* remediation

The following paragraph focuses on the crucial issue relative to the suitability of the different disinfectants for *Legionella* remediation.

Selected scientific literature showing the different efficacy of the three Cl-based biocides and support the statements depicted in Figure 1 is reported in the following Table 1.

Chlorine is the least effective chemical for *Legionella* remediation. This is due to the drawbacks previously discussed in this paper, which are primarily related to the chemical behavior of hypochlorous acid/hypochlorite ion, that are the two actual chlorine alternative chemical forms in aqueous media.

Despite its low cost as a chemical, chlorine, suffers high use costs for remediation due to its pH-dependency (active chlorine concentration is low at drinking water pH), corrosivity (Hassinen et al., 2004, Castagnetti et al., 2011) and stability (being highly reactive and thus not stable in hot water). Moreover, some publications highlighted the risk of a potential resistance of *Legionella* to chlorination thanks to the presence of biofilm (Cooper and Hanlon, 2010), and to the activation of intracellular stress adaptive processes (Bodet et al., 2012).

Chlorine dioxide could be a better choice compared to chlorine, (ensuring more effective and lasting remediation outcome), but it suffers several drawbacks, described here above, that limit its application.

It is a gas in solution and a hazardous chemical, principally produced, for drinking water application, by mixing sodium chlorite and hydrochloric acid: since chlorine dioxide is potentially explosive, the generation equipment must be designed to avoid this risk. Recently, 0.3%wt. chlorine dioxide stabilized solutions appeared on the market but the risk posed by the transportation and storage of this chemical must be carefully taken into account. Moreover, the major drawback that limits its application is corrosivity, as discussed more in section 4.

Conversely, the literature survey summarized in Table 1 clearly demonstrates that the best remediation results have been obtained by application of monochloramine, mainly in hot water only (see next section for the reason of this choice). As shown earlier, this efficacy is the result of some monochloramine most beneficial properties (electron sharing, stability, pH and redox potential functions, biofilm penetration ability, decay pathways). Only recently monochloramine has started being well understood and more widespread used. This could explain why it took some time for monochloramine to affirm itself as a superior biocide for secondary disinfection of building system.

Only in the last 15-20 years evidences about monochloramine usage as a potential disinfectant for *Legionella* remediation started to be available in the scientific literature (Kool et al., 2009, Gao et al., 2000, Hellefinger et al., 2003, Flannery et al., 2005). In 2005 Loret (Loret et al., 2005) and McCoy (McCoy et al., 2005) supported the effectiveness of monochloramine by scientific data and envisaged the need for a generator of this chemical, still not available on the market at that time. The difficulties in controlling monochloramine generation and concentration into the water systems were the major obstacles that have been solved by a patented technology (pat. No. 8444860 - Garusi and Garusi, 2009). It was as recent as 2011 (Lin et al., 2011, Kandiah et al., 2012) when the first commercial application was investigated and reported in the United States.

The author contributed to the development of the cited commercial system and its efficacy is now supported by strong scientific evidences (Casini et al., 2014; Duda et al., 2014; Coniglio et al., 2015a, 2015b, 2015c, Kandiah et al., 2012, 2013; Marchesi et al., 2011, 2012 2013). These evidence based investigations convinced Dr J.E. Stout (Duda 2014) to affirm that now “monochloramine is a viable option for hospitals considering disinfection for *Legionella* control”, since it has fulfilled all of the 4-step process of validation earlier proposed by the same scientist (Stout and Yu, 2003):

1. verification of efficacy using laboratory studies;
2. anecdotal field reports of efficiency from individual institutions;
3. controlled field trials in individual institutions;
4. successful applications in multiple institutions over a prolonged period.

Authors	Disinfection method	Concentration	Result
Helms C.M. et al., JAMA 1988	Chlorine	3-5 mg/l	From 29% to <5% positive sites after 5 years
Snyder et al., J Infect Dis 1990	Chlorine	2 -5 mg/l	From 37% to 7% positive sites after 17 months
Ditommasso S. et al., Infect Control Hosp Epidemiol 2006	Chlorine	2-3 mg/l	From 47% to 6% positive sites after 5 years
Hamilton E. et al., J Hosp Infect 1996	Chlorine dioxide	0.5–1 mg/l	From 28% to 12% positive sites after 6 months
Srinivasan A. et al., Infect Control Hosp Epidemiol 2003	Chlorine dioxide	0.8 mg/l	From 41% to 4% positive sites after 17 months
Scaturro M. et al., Infect Control Hosp Epidemiol 2007	Chlorine dioxide	0.4–0.5 mg/ l	Persistent colonization of water system
Casini B. et al., J Hosp Infect 2008	Chlorine dioxide	0.2–0.5 mg/ l	From 67% to 14% positive sites after 5 years
Hosein I.K. et al., J Hosp Infect 2005	Chlorine dioxide	0.5 mg/l	From 40% to 50% positive sites after 2 years
Zhang Z. et al., Infect Control Hosp Epidemiol 2007	Chlorine dioxide	0.5–0.7 mg/l	From 60% to 10% positive sites after 30 months
Sidari F.P. et al., AWWA Journal 2004	Chlorine dioxide	0.3 – 0.5 mg/l	From 27% to 3% positive sites in 1 month
Di Marino O. et al., EWGLI2007	Chlorine dioxide	0.2 – 0.3 mg/l	From 60% to < 5% in 1 month
Marchesi I. et al., AJIC, 2012	Monochloramine	2-3 mg/l	From 60% to 8% positive sites in 1 month
Kandiah S. et al., AJIC, 2012	Monochloramine	2-3 mg/l	From 33% to 0% positive sites in 3 weeks
Marchesi I. et al., J. Wat.Health. 2013	Monochloramine	2-3 mg/l	From 100% to 9.5% positive in 1 month
Kandiah S. et al., Infectious disorders, 2013	Monochloramine	2-4 mg/l	From 53% to 0.35% in 1 year
Marchesi I. et al., J. Wat. Health, 2013	Monochloramine Chlorine dioxide	2-3 mg/l 0.5-0.7 mg/l	From 100% to 9.5% in 36 months From 96% to 46% in 36 months
Casini B. et al., ICHE, 2014	Monochloramine	2 mg/L	From 100% to 0% positive within 1 month
Duda S. et al., ICHE, 2014	Monochloramine	1-4 mg/l	From 53% to an average of 9% in 30 months (sensor faucets risk evaluated)
Coniglio M. A. et al., J. Health. Sci. 2015	Monochloramine	2-3 mg/l	From 100% to 0% in 1 month

Table 1: literature survey on the efficacy of chlorine, chlorine dioxide and monochloramine in *Legionella* remediation

1.4 Unintended consequences of disinfection: no surprises if you know chemistry

The choice of a suitable water disinfection system should aim to achieve the most effective antimicrobial action, reducing at the same time the possible “side effects”: these are mainly related to by-products generation and corrosion issues.

If comparing the three chlorine-based disinfectants, many evidences highlight that chlorine generates much more toxic disinfection by-products (DBPs) than monochloramine: being a stronger oxidant, chlorine undergoes more redox reactions compared to monochloramine. Chlorine by-products are well known and regulated all over the world. The regulation is focused on THMs, but also includes chlorite and chlorate, haloacetic acids (HAA5), chlorinated organic molecules, bromide and bromate. This is the reason why many large municipalities in the US have adopted monochloramine to comply with the DBPR Stage 2³ regulation.

However, there are also some publications that describe unintended consequences of incorrect or uncontrolled monochloramination of drinking water (Symons et al., 1998; Mitch et al. 2003; Edwards et al., 2005), clearly pointing out the consequences of an improper monochloramine generation technology. Indeed, the incorrect or uncontrolled generation of monochloramine can lead to possible by-product generation. Most frequently, improper generation of monochloramine leads to ammonium ion or dichloramine but also THMs, haloacetic acid (HAA), and organic chloramines can be produced.

Particularly relevant is the problem of nitrosamines formation (for a more detailed analysis, see Section 3): N-Nitrosodimethylamine (NDMA), for example, can be produced by either chlorination or chloramination processes. Data collected and analyzed in a study published few years ago seems to suggest that, under particular circumstances, the levels of NDMA produced from chloramination are statistically significantly higher than those produced from chlorine. (Woods and Dickenson, 2015). However, the author extensive experience with monochloramine shows that NDMA formation is very unlikely under the proper method of generation and control of monochloramine (Garusi and Garusi, 2009). Accordingly, it was recently confirmed that, avoiding the presence of dichloramine, the production of NDMA by monochloramine is negligible (Selbes et al., 2018).

Chlorine dioxide main by-product is chlorite. Since the decomposition rate of chlorine dioxide is very high, particularly in hot water, the concentration of chlorite can be significantly high and overpass the maximum contaminant level (MCL) (0.8mg/l)⁴ for chlorite set in the US-EPA SDWA.

³ <http://www.epa.gov/dwreginfo/stage-1-and-stage-2-disinfectants-and-disinfection-byproducts-rules>

⁴ <http://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants#Byproducts>

Chlorine DBPs formation cannot be easily controlled by the simple addition of chlorine to water and further operations must be carried out to reduce DBPs concentration. DBPs minimization during monochloramination is easier than during chlorination since proper reaction conditions can be precisely established.

In order to obtain the right reaction conditions for monochloramine generation (Reaction 1) physical and chemical parameters must be controlled (Scheiber et al., 2005). Nowadays, the technology required to do that are well known and available on the market.

If the physical/chemical parameters are appropriately set, as represented in Reaction 1 the only theoretical by-product of monochloramine generation is water(!). However, since the real yield is lower than 100%, a small amount of free chlorine and free ammonia can be expected as the main side products.

Other possible side reactions are the formation of di- and tri-chloramine but, as already illustrated, they are favored at low pH (see Figure 5), which is uncommon in drinking water. The chemical composition of the reagents and the reaction chamber can be engineered to ensure optimal conditions for monochloramine formation.

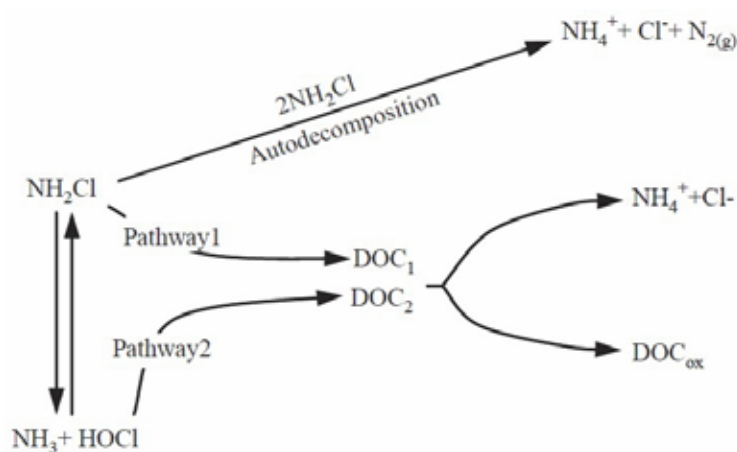


Figure 8: schematic representation of monochloramine reaction pathways in the presence of NOM. DOC_{ox} represents oxidized NOM (Duirk 2005)

It should be considered that THMs can be also produced in the chloramination process, by the reaction between free chlorine (hypochlorite) and natural organic matter (NOM) as in a standard chlorination process. Nonetheless, the formation of these by-products can be minimized by respecting the proper reagent addition order as already stated above (Scheiber et al., 2005). Moreover, the reaction rate of monochloramine formation is orders of magnitude greater than that of the THMs formation. This is the explanation for the lower THMs formation during chloramination.

According to all of these considerations, it is easy to understand that main by-product of the monochloramination reaction in drinking and domestic hot water loops is ammonium ion (NH_4^+) pro-

duced by monochloramine decomposition process when water consumption is low or negligible, for example overnight (see Figure 8).

The control of ammonium ion is mandatory to avoid potential nitrification and corrosion of copper piping (via the stable $[\text{Cu}(\text{NH}_3)_6]^{2+}$ coordination complex). The technology to do that is now available and ammonia residuals as low as < 0.2 ppm are not uncommon in properly controlled chloraminated water.

In conclusion, if correctly generated, monochloramine produces less DBPs than chlorine or chlorine dioxide and thus it is safely and reliably used for secondary disinfection of premise plumbing water systems.

1.5 The volatility issue

In the evaluation of the robustness and effectiveness of a disinfection solution, the volatility of the chemical adopted is another feature that should be taken into account.

Chlorine dioxide, being a gas in solution, has the highest volatility. Monochloramine and hypochlorous acid are nonetheless volatile compounds (Holzvarth et al., 1984), while hypochlorite, being an ion in solution is not. Since hypochlorite and hypochlorous acid are present simultaneously in drinking water (see Figure 4) and the fraction of hypochlorous acid depends on pH, the volatility of chlorine is much lower at drinking water pH range compared to that of monochloramine. This of course, could be a limitation in open air application, where flash off could be an issue, but not in the case of pressurized piped water. Additionally, even in the case of open drinking water storage tanks, the fraction of evaporated monochloramine is normally not an issue (after the first monochloramine molecules evaporate an equilibrium is established and the process stops). Moreover, being monochloramine far less aggressive than chlorine, the risk corrosion of wetted and air exposed components is greatly reduced.

1.6 Conclusions

Monochloramine belongs, together with hypochlorous acid/hypochlorite and chlorine dioxide, to the family of chlorine-based water disinfectants. The Cl atom is crucial for their antimicrobial activity and the specific properties that it acquires within each molecule explain the different behaviour and effectiveness of this disinfectant family members.

Produced starting from a chlorine precursor and an ammonium source, at the pH values typical of drinking water, monochloramine is the most favoured product of such a reaction. Thus, it does not suffer of the negative pH effect that conversely reduces hypochlorous acid/hypochlorite disinfection efficacy at pH higher than 7.

In the monochloramine molecule, the Cl atom is linked to a nitrogen atom: this partner mitigates the chlorine reactivity, making monochloramine a mild oxidant and a stable compound. These features allow it to be more effective in penetrating the biofilm, reaching and reacting against its actual target, i.e. bacteria. Indeed, several studies demonstrate that it represents an optimal secondary disinfection solution for *Legionella* remediation.

Due to its chemical properties, monochloramine is also capable of high persistence, ensuring the maintenance of effectiveness and proper concentration even in low flow regimes and in distal points of complex building water systems.

Even in terms of disinfection drawbacks, monochloramine is a cut above. When properly produced and dosed, it minimizes the generation of disinfection by-products, that by contrast can represent a serious concern for other disinfectant and for hypochlorous acid/hypochlorite in particular. Indeed, the only theoretical by-product of monochloramine synthesis reaction is water. Finally, its low oxidizing power makes it largely compatible with all the materials commonly used for piping systems, avoiding the occurrence of corrosion issues, frequently experienced with the use of the other chlorine-based disinfectants.

2

Some like it hot: cold vs. hot water considerations

2.1 *Legionella* in plumbing systems

Legionella remediation is one of the goals of building water system disinfection (ANSI/ASHRAE Standard 188-2015).

Legionellae, a gram-negative bacteria genus comprising over 60 known species (Euzéby, 2018), are ubiquitous in natural and artificial water environments worldwide and are able to survive in a range of environmental conditions (Fliermans et al., 1984). A significant number of these species are able to cause disease (generally known as Legionellosis), with a range of different implications from acute, self-limiting, influenza-like illness without pneumonia (Pontiac Fever) to severe pneumonia that, if untreated, can be fatal (Castillo et al., 2016). For these reasons, it is crucial to monitor its presence and contrast its proliferation in human-related water distribution systems.

The growth and the incidence of *Legionella* in premise plumbing systems is influenced by several different factors (Wadowsky et al., 1985). Some of these factors are pH, oxygen level, nutrients availability, temperature and the design of the plumbing system in the building. It has also been demonstrated that other microorganisms can favor *Legionella* proliferation; in particular, Protozoa represent an important vector for the survival and growth of *Legionella*, able to colonize and to proliferate within Amoebae. As related to plumbing system design, it is extremely important to apply good engineering practices to minimize dead legs and section of the pipes with low flow linear velocity, factors favoring the initial attachment and successive growth of bacterial biofilm synthesized by *Legionella* and other bacteria. In addition, the presence of tank water heaters the selection of the piping materials are other features that can influence the amplification of this opportunistic pathogen.

Even though the plumbing systems design and materials influence *Legionella* growth, the water temperature plays the key role in this unwanted process. As it will be more extensively discussed hereinafter, the optimum growth of this pathogen is found to be at ≈ 99 F (≈ 37 °C) (Wadowsky et al., 1988; Yee et al., 1982). However, live *Legionellae* have been isolated from hot-water systems up to ≈ 151 F (≈ 66 °C) and, even if the rate of reproduction decreases with decreasing temperature, it is shown that the bacterium is still able to grow at temperature $> \approx 68$ F ($> \approx 25$ °C) (Dennis et al., 1984; Wadowsky & Yee, 1983). For this reason, domestic hot water systems can provide a perfect environment for *Legionella* colonization.

The results reported in Table 2, show the influence of temperature and pipe material on the total flora and specifically on *Legionella pneumophila* (Rogers et al., 1994).

Temperature is known to have a deep impact on *Legionella* growth: the CFU/cm² of *L. pneumophila* is ≈ 30 times higher switching from 86 F to 104 F (from ≈ 20 °C to ≈ 40 °C) with PVCs pipes and ≈ 168 times with polybutylene pipes for the same temperature range.

Moreover, as represented in Figure 9, when temperature close to 104 F (≈ 40 °C) are reached in the

system, the number of *Legionella pneumophila* can increase from 1 Log CFU to almost 6 Log CFU within 5 - 6 days.

Temperature (°C)	Pipe Material	Colonization (CFU·cm ⁻²)	
		Total Flora	L. pneumophila
20	Copper	2.16·10 ⁵	0
	Polybutylene	5.70·10 ⁵	665
	PVCs	1.81·10 ⁶	2,132
40	Copper	5.70·10 ⁴	1,967
	Polybutylene	1.18·10 ⁵	111,880
	PVCs	3.67·10 ⁵	68,379
50	Copper	2.26·10 ⁴	0
	Polybutylene	3.21·10 ⁶	868
	PVCs	1.22·10 ⁵	60
60	Copper	4.47·10 ²	0
	Polybutylene	4.25·10 ⁴	0
	PVCs	5.19·10 ³	0

Table 2: Effect of temperature and pipe material on the total flora ad *L. pneumophila* colonization.

At temperatures above 122 F (≈ 50 °C) the pathogen cell number starts to decrease; however, it does not mean that this high temperature ensures a complete elimination of *Legionella* risk. Indeed, some of the bacteria can survive at even higher temperatures when protected by biofilm (Dennis et al., 1984).

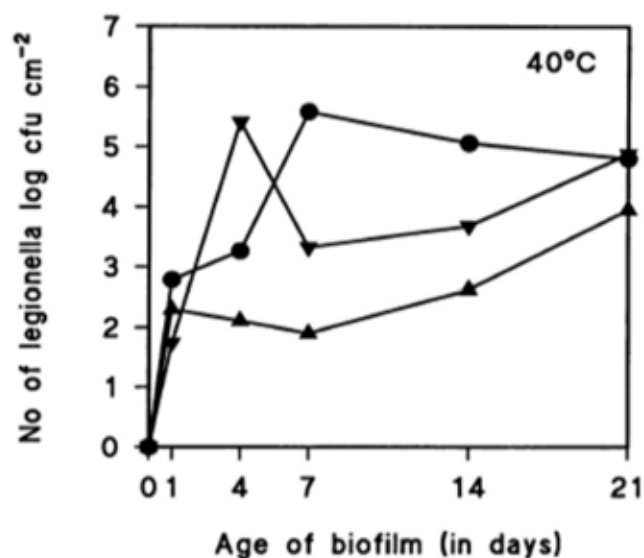


Figure 9: growth of *Legionella pneumophila* measured experimentally at T= 40 °C and with different pipe materials. Circle: Polybutylene; Up-Triangle: Copper; Down-Triangle: PVCs (Rogers et al., 1994).

This strong relation between *Legionella* colonization and system temperature has linked the occurrence of this waterborne pathogen with hot water system in nearly 85% of the cases where *Legionella* was found (Ruf et al., 1988; Tadashi et al., 2006).

2.2 Supplemental disinfection remediation treatments

The municipal water treatment plants usually use chlorine as disinfectant to kill bacteria. However, this disinfectant is an oxidizing agent and its decay rate can lead to very little disinfectant residual in the water that enters the buildings. For this reason, chlorine or monochloramine are often used as secondary disinfectant. The secondary disinfection aim is to keep a consistent disinfectant residual in the water that goes from the treatment plant through distribution to the building, in order to avoid the growth of bacteria at distal points.

Since the risk of Legionellosis is directly related to the presence of *Legionella* cells in the water system, healthcare facilities (hospital, nursing homes), hospitality (hotels, casinos) and condominium complexes are more and more concerned about this pathogenic threat. For this reason, the installation of on-site supplemental disinfection treatment units has become more widespread in recent years with the aim to reduce the risk of proliferation of bacteria that survive the first two steps of municipal disinfection. EPA listed biocides used as supplemental disinfectants under the Safe Drinking Water Act are chlorine (HClO), chlorine dioxide (ClO_2) and monochloramine (NH_2Cl).

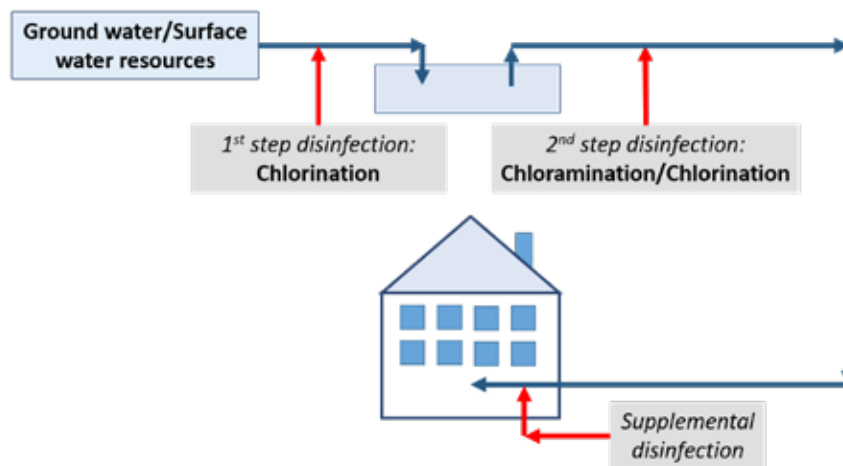


Figure 10: Typical scheme from municipality treatment plants to building supplemental disinfection.

The type of on-site disinfectant chosen plays a fundamental role in the control of *Legionella* and other waterborne pathogens throughout the building. However, it is important to remember that the effect of the disinfectant is not limited to *Legionella* control but, based on the chemistry of the biocide, it can also have a significant impact on the plumbing system (corrosion issues) and bring to the formation of unwanted disinfection by-products (DBPs). In the light of current scientific knowledge, monochloramine has proven to be the most suitable disinfectant that can be applied for supplemental disinfection: 1) it is effective at a residual of 2-3 ppm (mg/L) and, due to its stability as a combined chlorine species, is more effective than other oxidizing bioci-

des; 2) if correctly produced, monochloramine does not generate disinfection by-products and 3) it is minimally corrosive compared with chlorine and chlorine dioxide (Marchesi et al., 2016). Its high stability also allows it to better penetrate biofilm without reacting out at its surface, leading to a more complete and efficient disinfection (Treweek et al., 1985; Le Chevallier et al., 1993; McNeill et al., 2001).

2.3 How and where apply supplemental disinfection to ensure a better efficacy

As explained in the previous paragraph, the choice of disinfectant plays a crucial role on the effectiveness against *Legionella*. However, this is not the only factor influencing the success of the supplemental disinfection: the design of the generator unit, how it is plumbed and in which system it is connected are also factors that must be taken into account when speaking about supplemental disinfection.

Since it is known that *Legionella* colonizes primarily in warm water, one of the most asked question is: should just the hot water of the building be treated or should the entire cold water coming into the facility (which includes both cold and hot water) be treated? Alternatively, as a last option, should two different supplemental water treatment units be installed, one on the main cold line and one on the hot water system?

At a first glance, it may seem preferable to add the disinfectant to all the water coming into the building, but unfortunately there is not a universal answer to this crucial question. The decision in treating either the hot water system or the entire plumbing system (or both) should be taken considering three main factors: the chemistry, the microbiology and economics of the alternatives.

Chemistry

Different disinfectants have different physical chemical properties, and the temperature of the water in which the biocide is dosed plays a crucial role for its efficacy.

Temperature strongly influences the disinfectant decay rate. Higher temperature leads to a faster decay. This effect is stronger for chlorine and chlorine dioxide since these biocides are known to be unstable, even at low temperatures. An increase in water temperature from 70 F ($\approx 21\text{ }^{\circ}\text{C}$) to 120 F ($\approx 49\text{ }^{\circ}\text{C}$) decreases the half-life time (time to half the biocide concentration) from 20 h to 10 h and from 12 h to 5 h for chlorine and chlorine dioxide respectively (Ammar et al., 2014; Fischer et al., 2012; Hua et al., 1999). Monochloramine is a more stable oxidizer, so the half-life time would be decreased from 200 h to 100 h with the same increase in water temperature from 70 F to 120 F. In the cases of chlorine or chlorine dioxide, this lack of stability will make the diffusion process to all the fixtures and the faucets in the building difficult. In addition, if the biocide feed would be discontinued for any reason, the building/facility pipe system would remain without a consistent biocide residual within few hours.

Another important chemical factor related to the water temperature is the “thermal shock” at which the disinfectant would be subjected if fed in the cold water system. After the dosing point

in the main cold line, even if just a small portion, part of that water will flow through the water heaters at some point. This step will quickly increase the water temperature up to $\approx 140\text{-}150$ F ($\approx 60\text{-}65$ °C). Such a sudden temperature increase would have a negative effect on the disinfectant stability and the consequent degradation of the biocide could produce DBPs as THMs, HAA5, chlorites and free ammonia; moreover, it determines a strong reduction of active biocide concentration. If the supplemental disinfection unit is installed only on cold water it could be a serious threat for what concerns DBPs issue since the formation of by-products wouldn't be controlled in the hot water system/s. For this reasons, if the disinfectant is added just in the cold water line, some solutions must be taken into account to reduce and control the formation of by-products in the hot water loop and to maintain a consistent biocide residual within it. A possible and simple solution could be to install purge valves in the hot loop/s and purge them for a certain amount of time in order to reduce the water age in the system. These purge valves could be driven by different parameters as time, ORP and oxidant level (total and/or free chlorine). Another by-products control system, applicable when monochloramine is used and fed in the main cold water line, can allow the recombination of free ammonia residual present in the hot water system back to monochloramine by feeding a chlorine-based solution in the hot water loop/s. This last option ensures a better environmental impact because no water is discharged and new fresh disinfectant is formed in the system.

The design and the type of biocide dosage into the system are other important factors. When the biocide generator is installed in the hot system, the water is always circulating thanks to the return pumps. This means that even though there is no hot water consumption, i.e. during night hours, it is possible to trim the disinfectant production if needed and add it into the system by monitoring oxidant levels. The biocide, once generated, can be injected into the hot water supply and immediately diluted and distributed into the whole recirculated hot water system. This type of production trimming cannot be done in case of cold water installations since the disinfectant is generated only when new water is flowing, so no precursors can be added to maintain a consistent residual in no-flow conditions.

Microbiology

As easily predictable considering the core temperature of the human body, ≈ 98 °F (37 °C), normal human microbiota and pathogens (e.g., *Lactobacillus spp.*, *E. coli*, *Salmonella spp.*) are mesophiles: they are adapted to moderate temperatures, with optimal growth temperatures ranging from room temperature ≈ 70 F (≈ 20 °C) to ≈ 113 F (≈ 45 °C) (Elliot et al., 2002). Similarly, as a thermo-tolerant pathogen, *Legionella* does not proliferate efficiently at temperatures typical of cold water < 70 F ($< \approx 20$ °C). For this reason, treating all the cold water that comes into the building/facility not only is often unnecessary to reduce the risk of Legionellosis, but could also present some microbiological issues. In particular, monochloramine degradation process driven by water heating step can cause an increase of free ammonia concentration: this could lead to proliferation of nitrifying bacteria like *Nitrosomonas spp.* that, ultimately, could create favorable

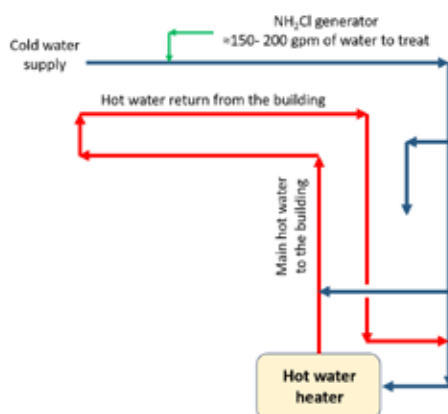
conditions for other bacteria (mycobacteria and coliforms) growth, as reported by Pryor et al., 2004. If, for any reasons, monochloramine disinfection of cold water main line is required, it is important to consider the biocide degradation during the heating step and apply one of the solutions proposed above, i.e. install purge valves in the hot loop/s and purge them to reduce water age in the pipes or, even better, recombine the free ammonia residual present in the hot water system back to monochloramine by feeding a chlorine-based solution in the hot water loop/s. However, where possible, dosing monochloramine on hot water is preferable because not only it has been reported that, if monochloramine concentration is constantly maintained above 2 ppm no bacterial growth should be observed in hot water (Marchesi I. et al., 2013; Duda et al., 2014; Casini et al., 2014), but also it reduces the risk of nitrification since nitrifying bacteria are less likely to colonize in temperature environment typical of hot water system.

In conclusion, since *Legionella* does not colonize and populate cold water systems, from a microbiological point of view, it is possible to get an effective remediation by supplying monochloramine in hot water only, as previously reported by several independent works (Casini et al., 2014; Duda et al., 2014; Coniglio et al., 2015a, 2015b, 2015c; Kandiah et al., 2012, 2013; Marchesi et al., 2011, 2012, 2013).

Economics

Chlorine and monochloramine demonstrated to be effective against *Legionella* at residuals between 2 - 3 ppm (Coniglio et al., 2015) while chlorine dioxide is effective at concentrations between 0.5 - 0.7 ppm (Zhang et al., 2009). The disinfectant concentrations required are the same regardless of whether the biocide is injected in the cold or in the hot water, but the difference obviously lies in the volume of water to be treated. In hundreds of applications in Europe and in the US, it has been demonstrated that the hot water usage into a building is about 6 - 10% of the total water. It follows that 10 - 12 times more biocide has to be generated, and 10 - 12 times the amount of chemicals have to be stored and used, if all the incoming cold water is to be treated.

Cold water diagram:



Hot water diagram:

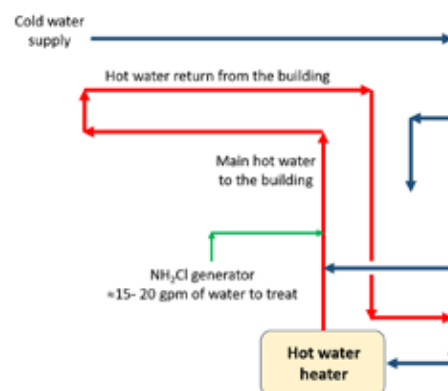


Figure 11: Cold and hot water diagram installation.

Two simple cold and hot water installation diagrams are reported in Figure 11.

The increased amount of reagents required for total cold water system leads to an increase in the operating costs and to possible storage problems. Also, bigger generator units have to be designed and installed, increasing the capital cost of the disinfection process. As an example, to treat hospitals and nursing homes hot water systems, disinfectant generator units capable to produce just few grams per hour of biocide are usually enough. By contrast, if all the incoming cold water has to be treated, units capable to produce hundreds of grams per hour of disinfectant are needed.

Other factors

Beside to the previous reported issues, of course other driving factors have to be considered. One of them is the specificity of international, and moreover national, regulations. In the case of US, for example, each State in the Country has its own regulations about water disinfection so it's not hard to run into applications in which the State's Regulatory People specifically require to treat either just the cold system or both of them.

Another side factor that influences the choice about the installation of a suitable disinfection unit is the design of the plumbing system. The final aim of the application of a supplemental disinfection unit is to minimize the risk of *Legionella* proliferation but always ensuring, at the same time, a cost effective solution. For several plumbing systems, this could turn to be a hard job. Especially in old buildings, the plumbing systems could be improperly designed. For example, some facilities could have multiple hot water loops so that would increase too much the capital cost to treat all of them. In such situation, treating all the incoming cold water on the main line would seem to be the best solution. On the other hand, sometimes the main cold line feeds also chillers and cooling towers that already have their own disinfection treatments so treating all the incoming cold water is not necessary, and the best design would be to treat the hot water loop only.

2.4 Conclusions

Supplemental disinfection units are applied in building water system in order to ensure a consistent disinfectant residual in the buildings pipes. The type of disinfectant chosen plays a crucial role on the efficacy of the disinfection treatment. A key factor that affects the *Legionella* remediation process is the temperature of the water where the disinfectant is applied. In other words, the choice to feed the disinfectant either on the main cold water line or on the domestic hot water loop (or both) becomes extremely important. The main factors that influence this important decision are related to the chemistry, the microbiology and the economics.

From a chemistry standpoint, higher temperatures could increase the decay ratio of the disinfectant. Thus, if the disinfectant is injected in the cold line, part of the treated water will flow through the water heaters and the “thermal shock” at which the biocide is subjected could breakdown the molecule, reducing its concentration and increasing the potential formation of harmful disinfection by-products. Injecting the disinfectant in the domestic hot water loop helps to control by-product formation and ensure a better dosage control because the water is always circulating into the system even when nobody is using hot water (i.e. during night hours).

Microbiologically, *Legionella* colonizes primarily in hot water, therefore treating all the cold water system would be useless and could also modify the microbiological environment with the potential risk of an increase of mycobacteria and coliform bacteria.

Economically, treating the entire building plumbing system would increase the equipment and operational costs since bigger disinfection units have to be installed and bigger volume of reagents are going to be consumed. This last consideration could be also a safety threat because bigger volumes of chemical must be stored on site.

These are only the three main factors to take into account when applying a supplemental disinfection system and also other driving forces have to be considered as a part of the decision process, such as states regulation and plumbing systems design and materials.

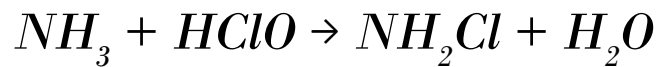
3

**Everything you've wanted to know
about NDMA formation**

3.1 A brief focus on monochloramine disinfection

Monochloramine (NH_2Cl) is the most effective Cl-based disinfectant and is also the most respectful toward materials. It is effective at a concentration of 2-3 mg/l, that can attain a 0% colonization within a few weeks of continuous application. Thanks to its stability, it is very effective in complex building plumbing systems.

As already described in Section 1, monochloramine is synthesized from hypochlorous acid and ammonia or an ammonium salt (usually chloride or sulfate) as follows in Eq. 1:



Reaction 4: monochloramine formation

During this reaction, other chloramines could be formed (di and tri chloramines, respectively NHCl_2 and NCl_3). pH plays a key role in determining which specie is produced: monochloramine is very stable and is the predominant species at a pH above 7.2. In this conditions, dichloramine and trichloramine cannot form.

Monochloramine has a low oxidant power with respect to other chlorine-based disinfectants, due to its lower oxidation potential (ORP). This is not a drawback, however, because stability and low reactivity help monochloramine to better penetrate biofilms and kill bacteria inside the biofilm. This is also one of the reason why monochloramine is a suitable biocide for secondary disinfection (especially in domestic hot water loops) where long contact time between the biocide and the bacteria can be achieved. This feature is very useful to keep out contamination in dead legs during commissioning, renovation or intermittent use. Monochloramine stability creates an opportunity to have the correct biocide concentration in all the pipes of the building even in low flow regimes, such as oversized pipes, temporary dead legs, and varying flow situations where other biocides fail.

Moreover, monochloramine proved to be less aggressive towards pipe materials (Treweek et al., 1985; Le Chevallier et al., 1993; McNeill et al., 2001), also thanks to several tests carried out by the Authors on different pipe materials like copper, galvanizer iron, stainless steel, PEX, PPR and C-PVC.

By contrast, due to the higher oxidant power, chlorine attacks pipe materials (both metals and plastic) causing corrosion issues. Boffardi (Boffardi et al., 1992) showed that at concentrations above 0.5 ppm chlorine leads to iron corrosion in drinking water piping, while it has been more recently (Hassinen et al., 2004; Castagnetti et al., 2010) demonstrated that chlorine is also corrosive on PE (polyethylene) and PP (polypropylene) pipes which are becoming more and more common for water distribution piping.

3.2 Disinfection by products: what we need to know

Disinfection byproducts (DBPs) are the result of chemical reactions between organic/inorganic matter in water and the chemical treatment agents during the water disinfection process (Richardson et al., 2007). Typical DBPs are trihalomethanes (THMs), haloacetic acids (HAAs), organic chloramines and nitrosamines. The World Health Organization (WHO) has established guidelines for several DBPs since some of them are classified as possible human carcinogens. However, The WHO has stated that "the risk of death from pathogens is at least 100 to 1000 times greater than the risk of cancer from disinfection by-products (DBPs)" and that the "risk of illness from pathogens is at least 10000 to 1 million times greater than the risk of cancer from DBPs" (Nieuwenhuijsen et al., 2009).

If monochloramine and traditional chlorine disinfectants are compared in terms of DBPs formation, NH_2Cl produces less disinfection by-products. Higher concentration of THMs and HAAs were found when traditional chlorine-based disinfection technologies were used. For this reason, during the recent years an increasing number of drinking water utilities are switching from traditional chlorination to chloramination in order to fully comply with the US Environmental Protection Agency's (USEPA's) Stage 2 Disinfectants and Disinfection Byproduct Rule (D/DBPR) (Kiari et al., 2017).

However, as discussed in Section 1, some scientific papers demonstrated how an improper or incorrect dosage of NH_2Cl and/or monochloramine precursors could lead to the formation of disinfection byproducts. These byproducts are mostly ammonium ion and dichloramine. In some cases, also the presence of organic chloramines was detected (Symons et al., 1998; Mitch et al., 2003; Edwards et al., 2005).

Within the last years particular attention has been given to the compounds defined as "nitrosoamines" (Kiari et al., 2017). These molecules are organic chloramines but with a group $(\text{R})_2\text{N}-\text{N}=\text{O}$ linked to the ammonia nitrogen atom. The most common nitrosamines are NDMA, NDBA, NDEA, NDPA, NEMA, NMOR, NPIP and NPYR. These molecules are reported in Figure 12.

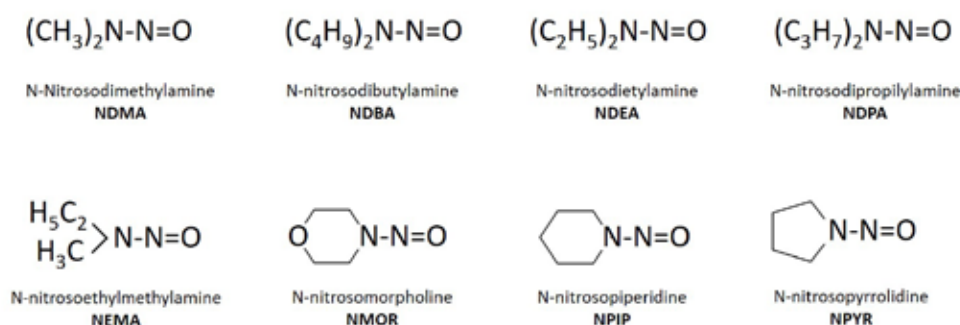


Figure 12: Most common nitrosamines.

Five nitrosamines were listed on the third and fourth SDWA Contaminant Candidate Lists: NDEA, NDMA, NDPA, N-nitrosodiphenylamine and NPYR, indicating that USEPA is considering these contaminants for potential regulatory determination. Some studies demonstrated that NDMA is the most frequently detected nitrosamine in water after disinfection processes (Russel et al., 2012; Linge et al., 2017). Figure 13 reports the detected level of different nitrosamines after a disinfection process carried out on a surface water; it is clear that NDMA was the nitrosamine specie with the highest concentration value.

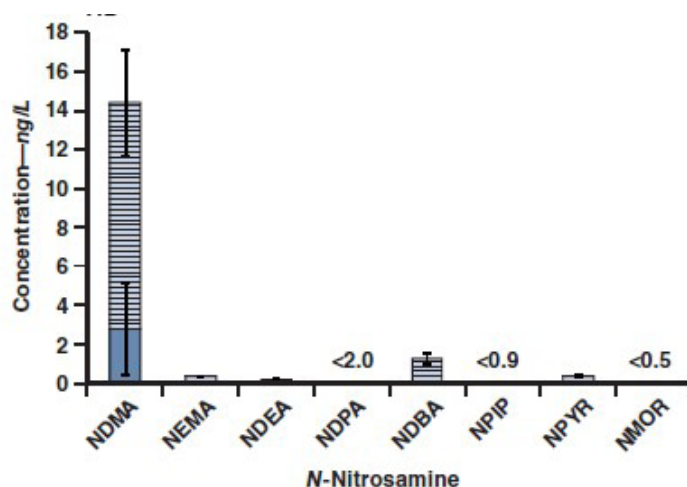


Figure 13: Different concentration of nitrosamines after water disinfection on a surface water. (Linge K. et al., Journal AWWA, 2017, 109, 184-196).

As a result, California's Department of Public Health did set a 10 ng/L notification level for three nitrosamines: NDEA, NDPA and NDMA (Russel et al., 2012).

Several scientific researches have been focused on the cause of the formation of nitrosamines, and in particular NDMA, by carrying out different tests, analyses, case studies and data collection from a huge number of water treatment plants. The results were compared as a function of different criteria, such as the type of chemical treatment applied, the type of water treated (surface of ground), the presence of filters, active carbon etc.

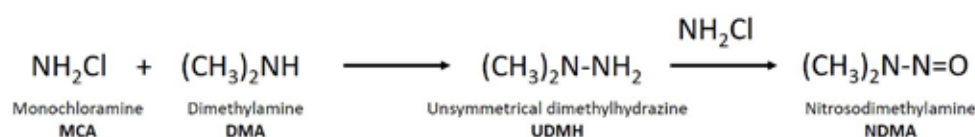
Taken together, the results of these studies suggest that monochloramine itself is not directly involved in the chemical process that leads to the formation of NDMA. As a weak oxidant, NH_2Cl performs its function as a biocide by killing bacteria and removing biofilm while preserving the piping construction materials. The formation of NDMA is not chemically involved in this biocidal action path. There are two main hypothetical chemical reactions that leads to NDMA generation. In the first reaction path, proposed by Choi (Choi et al., 2002) monochloramine reacts with dimethylamine to produce unsymmetrical dimethylhydrazine (UDMH). This species is then further oxidized by monochloramine to NDMA.

The reaction path proposed by Choi was then further revised by Schreiber and Mitch (Schreiber

and Mitch, 2006). They investigated the process more deeply in order to identify the correct chemical reactions. In particular, they demonstrated the critical importance of dichloramine and dissolved oxygen in the process. In fact, in this new approach it was confirmed that dichloramine reacts with secondary amine precursors to form chlorinated unsymmetrical dialkylhydrazine intermediate. This intermediate specie is then oxidized to NDMA by the oxygen molecules that are dissolved into the water.

Moreover, in their work, Schreiber and Mitch carried out tests using monochloramine as a possible precursor of NDMA and they demonstrated that the NDMA that was formed was due to the presence of dichloramine impurities instead of NH_2Cl itself.

Path 1, proposed by *Choi* (2002):



Path 2, proposed and confirmed by *Schreiber and Mitch* (2006):

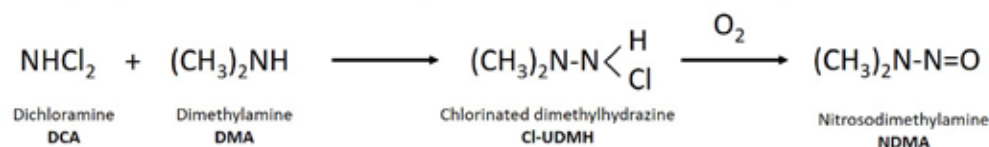


Figure 14: Old (1) ad new (2) hypothesis for NDMA formation.

The NDMA formation scheme proposed by Choi and the revised version confirmed by Schreiber and Mitch are reported hereinafter in Figure 14.

The path proposed by Schreiber and Mitch confirms that monochloramine is not involved into the NDMA formation process. Despite the fact, some researchers still suggest a linking between the presence of NDMA and the use of chloramination process for water disinfection.

3.3 Back to the chemistry of monochloramine

In order to better understand why monochloramine cannot be responsible for the generation of NDMA and other nitrosamines it is important to take a look again on the chemistry related to this molecule.

As reported in Reaction 3, monochloramine is generated by two different precursors, a chlorine based compound and ammonia or ammonia precursors like ammonium salts. This chemical reaction is very fast, and has a rate constant that is equal to $k_{\text{NH}_2\text{Cl}} = 1.5 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Morris et al., 1981). Such a high number suggests that once monochloramine precursors come in contact, NH_2Cl is generated faster than any by-products, such as dichloramine and free ammonia, since the kinetic constant of other reactions are, at least, three orders of magnitude smaller.

Factors that influence monochloramine formation are temperature, reagents concentration, N/Cl ratio and pH. This latter is one the most important parameter to keep under control during a chloramination process: the pH value of the water plays a key role in the equilibria between hypochlorous acid (HClO) and its dissociated form, the hypochlorite ion (OCl^-).

The equilibria between the two species, referred as % of HClO available, is presented in Figure 15.

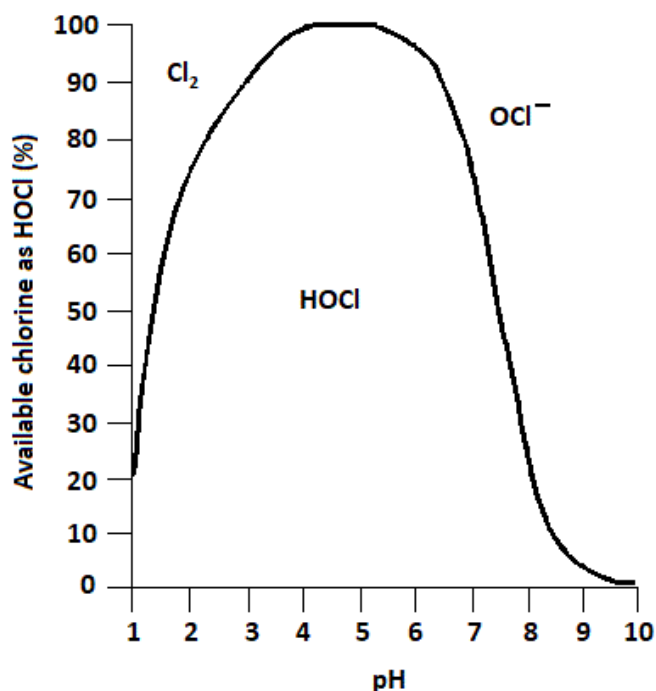
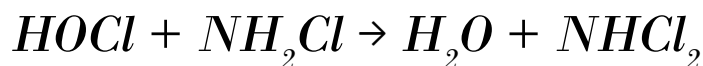


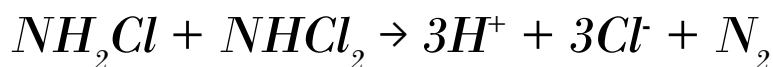
Figure 15: Chlorine, hypochlorous acid and hypochlorite ion equilibria at different pH values.

As already reported in Section 1, the optimal pH for monochloramine formation during a chloramination process is above 7.2. Over this point, the % HOCl available into water leads to the formation of only monochloramine, and completely suppresses the formation of di- and tri-chlorinated compounds. At pH value lower than 7.2, in addition to NH_2Cl production, the greater % of HOCl could favor the dichloramine formation, as depicted in Reaction 5:



Reaction 5: dichloramine formation

Monochloramine is then susceptible to degradation driven by dichloramine. This oxidation reaction leads to the formation of gaseous nitrogen, through the following reaction Reaction 6:



Reaction 6: monochloramine decomposition

Moreover, this reaction produces an acid species (dissociated HCl) which additionally lowers the pH value, thus favoring a further formation of dichloramine due to the high presence of non-dissociated HOCl in the solution. These reactions explain how an improper control of the pH value during a chloramination process could lead to the formation of dichloramine, which has been proven to be one of the two NDMA precursors.

In addition to the preferential production at pH values typical for drinking water, monochloramine can also take advantage of better chemical stability than traditional chlorine. Vikesland (Vikesland et al., 2001) carried out some experimental works to determine the stability of monochloramine and the decay of this molecule over time in different conditions (pH, monochloramine concentration and CO_3^{2-} concentration).

In Figure 16-A, the stability of monochloramine over time was evaluated at different starting concentrations (time zero concentration) of the biocide. In drinking water range, where monochloramine concentration is of about 2-3 ppm (0.05 mM), monochloramine value remained stable for the whole duration of the test (≈ 170 h). Only concentrations higher with respect to the drinking water range (> 5 ppm) resulted in a small loss of NH_2Cl during the test.

Figure 16-B, illustrates the stability of monochloramine at different pH values. At low pH (= 6.55) a drop in the NH_2Cl concentration was observed during the test, since at pH lower than 7.2, monochloramine is not the most stable molecule in the chloramine family. However, the higher the pH, the greater the NH_2Cl stability over time. At pH= 7.56 a loss of only 0.5 ppm in ≈ 170 h was measured due to hydrolysis reaction, while at pH= 8.34, monochloramine was completely stable over the whole duration of the test.

Figure 16-C shows the influence of the total carbonate concentration on monochloramine stability.

ty. These tests were carried out since the presence of acid catalysts as phosphate, sulfate, and acetic acid can accelerate monochloramine decay by catalyzing monochloramine disproportionation reaction. Carbonate ions (CO_3^{2-}) could act as an acid catalyst dependently on the pH level, since at low pH values the dissociation equilibrium of carbonic acid is left shifted, and acid species are present (carbonic acid and mostly bicarbonate at pH between 7- 8).

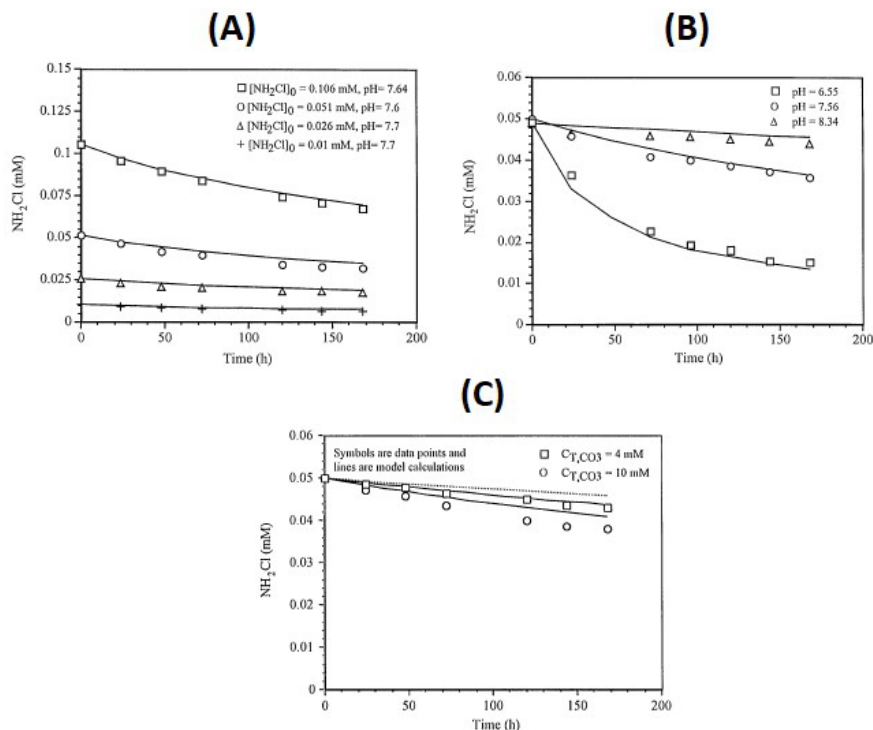


Figure 16: Monochloramine stability over time at, (A): different NH_2Cl concentrations, (B): different pH, (C): different CO_3^{2-} concentrations (Vikesland P. J. et al., Water Resources, 2001, 35, 1766-1776).

In drinking water range, as shown in Figure 16-C (pH \approx 8) monochloramine is almost unaffected by the presence of carbonate species. Only a decrease of about 0.5 ppm was measured when high concentrations of carbonate (10 mM) were present.

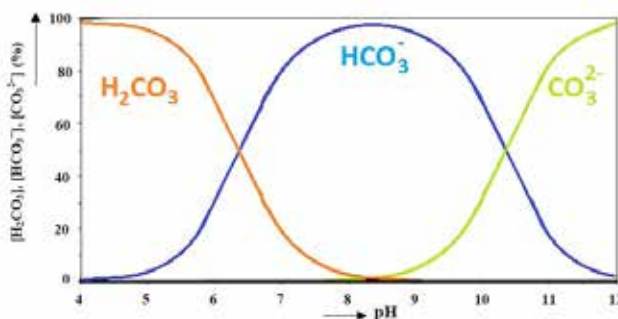


Figure 17: Distribution of the carbonic fraction as percentages of the total carbon content at different pH (Greenwood et al., Chemistry of the Elements (2nd ed.). Butterworth-Heinemann, 1997, ISBN 0-08-037941-9).

The results reported in Figure 16-A-B-C confirm that monochloramine is a stable molecule in drinking water parameters ranges. This is another confirmation that monochloramine cannot be directly responsible for NDMA formation.

Another extremely important parameter during monochloramine formation, is the Cl/N ratio. This ratio between the two reagents (a chlorine base compound and an ammonium salt) must be set in a proper range in order to avoid the presence of side reactions and/or the complete nitrogen components oxidation, also called breakpoint reaction. The effect of chlorine to nitrogen ratio is shown in Figure 18.

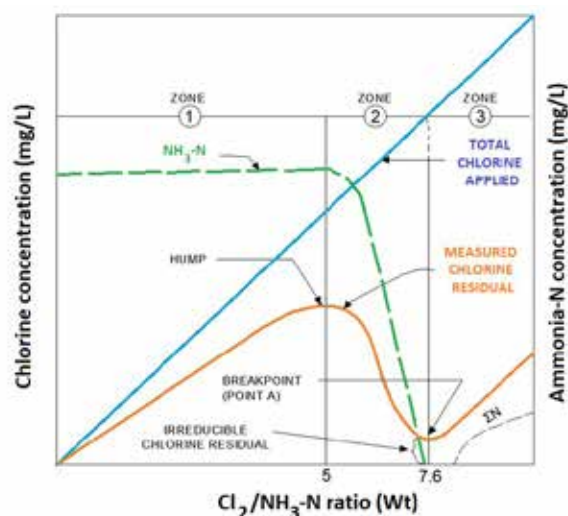


Figure 18: Breakpoint curve (Saunier B. M. et al., Journal AWWA, 1979, 71, 164-172).

Initially, chlorine residual (orange line) increases in the monochloramine region up to a $\text{Cl}_2/\text{NH}_3\text{-N}$ weight ratio equal to 5 (zone 1). With additional chlorine, the measured chlorine residual (orange line) and the available ammonia (green line) decrease, with the formation of dichloramine until a chlorine to nitrogen weight ratio of 7.6 is reached (zone 2).

At this point chlorine oxidizes all the possible chemical species, and it is termed “breakpoint”. Further chlorination after the breakpoint leads to an increase in the measured free chlorine. The disinfection technique based on the addition of free chlorine after the 7.6 weight ratio is called “breakpoint chlorination” (zone 3).

3.4 Why is there NDMA occurrence in municipal water treatment plants?

The main two water sources can be classified as surface water resources and ground water resources. The first one include rivers, lake and smaller water streams, while the second are all those sources that come from the underground, like aquifers.

Water goes through several chemical and physical treatments during the purification process: anticoagulant agents are added, pH level is adjusted and filtration steps are carried out. Of course, a disinfectant process is needed, in addition, to reduce the bacterial content in water.

The two main types of disinfection adopted in the US are traditional chlorination, where free chlorine is used as a biocide, and chloramination, where monochloramine is generated and exploited to kill bacteria. In both of them, the first step of the disinfection process involves a chlorination disinfection by feeding chlorine into the water. This is called “primary disinfection”. After this point a second addition of disinfectant is applied to avoid bacterial re-growth. This second biocide injection is called “secondary disinfection”. In traditional chlorination plants the secondary disinfection step is carried out by feeding additional chlorine, while in chloramination water utilities ammonia is injected into the water in order to react with the residual chlorine and form monochloramine.

A simple layout of an municipal chloramination process is presented in Figure 19.

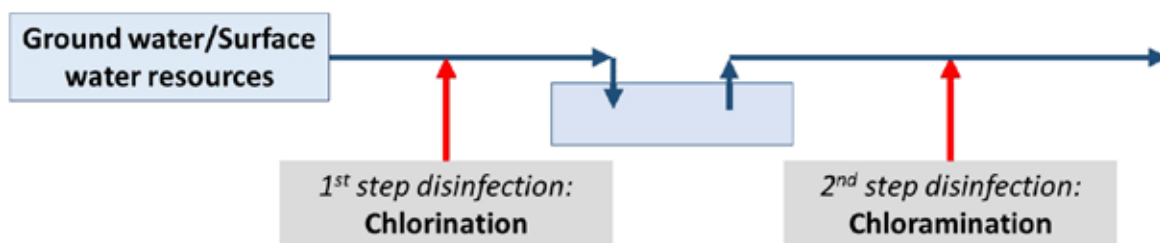


Figure 19: Scheme of an industrial chloramination process.

Woods (Woods et al., 2015) carried out a study in which NDMA levels were measure and monitored in different water treatment plants all over in the USA. The author highlighted how the use of a chloramination process for water disinfection was linked to the presence of NDMA in water after the biocide generation. In particular, the 48 % of the utilities that were using monochloramine were found positive to NDMA testing, while in only 3.8 % of chlorine based water treatment plants NDMA was detected.

It is then important to understand why traces of NDMA were found in municipal chloramination water treatment plants since it has been demonstrated that monochloramine is not directly responsible for NDMA formation.

The first consideration that has to be taken while reading the results presented by Woods and Dickenson, is the relation between the occurrence of nitrosodimethylamine and the type of water source that is fed to the plant. In particular, NDMA levels were measured and the results of water disinfection plants treating either surface water or ground water were compared. Data suggested that groundwater, as a source water, had a 3.3% frequency of occurrence of detectable NDMA, while surface water plants had 23 % occurrence of detection in all the utilities tested. This trend was also confirmed by Linge (Linge et al., 2017) in a study in which NDMA levels in surface and groundwater treated with chloramine in western Australia were analyzed. The result showed that NDMA was much more likely to be found in surface water resources.

The reason why ground water resources generate much less NDMA with respect to surface water is due to the lack of organic species. These organic species are not only classical organic molecules, but also organisms that over a long period of time can decompose into organic compounds that can lead to NDMA formation: the greater presence of animals, organisms, and also of dissolved oxygen into surface water resources, the more suitable the environment for NDMA precursors formation.

Moreover, by looking at the chemistry of monochloramine it should be considered that an improper generation of this biocide could lead to the formation of dichloramine, that further reacts with the other ammonia based compounds present in surface waters to form NDMA.

As explained in the previous paragraphs, monochloramine is a powerful disinfectant which has great biocidal power and advantages compared to other oxidizing disinfectants. But, it also has a delicate chemistry. For this reason, during a chloramination process all the chemical parameters must be respected in order to avoid unwanted surprises during the monochloramine formation. If NH_2Cl is properly generated (Garusi and Garusi, 2009) no NHCl_2 is formed, and the formation of NDMA is therefore impossible. During a chloramination process the reagents must be added with a stoichiometric precision in order to make the chlorine and the ammonium precursors react with a complete selectivity toward monochloramine. Also, the pH value has to be in the appropriate range.

In a municipal water treatment chloramination plant, where a huge volume of water is treated and ammonia is added after chlorine, it is difficult to keep the same standards as in smaller applications. For this reason, it is possible that in some areas of the treated water the proper stoichiometric ratio between the two reagents is not respected: in this case, dichloramine can be produced.

After taking these other factors into consideration it is clear that the real problem concerning NDMA in water treatment plants is the presence of organic precursors. For this reason, a lot of

attention has been given to the type of treatment and what solutions might be found to remove and/or inhibit the generation of these molecules.

Recently, Uzun (Uzun et al., 2017) evaluated the reduction of the NDMA formation potential by carrying out different experimental tests to evaluate the varying effects of several aspects on the generation of NDMA, such as the different type of polymers used as flocculation aids, the impact of alum clarification, the effect of filtration, reverse osmosis, and pre/post oxidation treatments. Cornwell (Cornwell et al., 2017,a and 2017,b) carried out two different studies for the evaluation of different natural polymers in water treatment in order to replace synthetic polyDADMAC (and possibly alum), since this chemical proved to contribute to NDMA precursors.

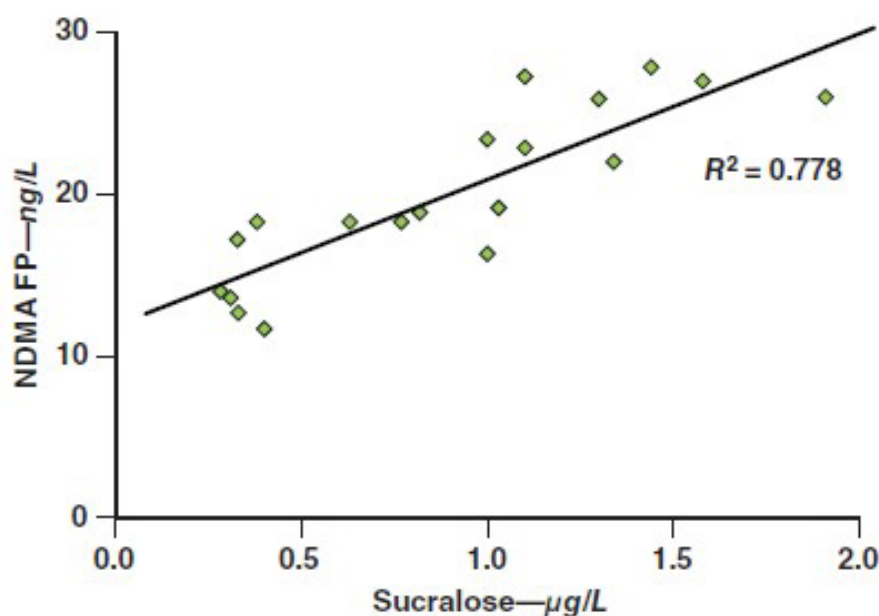


Figure 20: Relationship between sucralose concentration in wastewater treatment plants and NDMA formation potential (Prescott M. et al., Journal AWWA, 2017, 109, 243-251).

Also, Prescott (Prescott et al., 2017) highlighted how wastewater treatment plants are the major source of precursors for the formation of NDMA.

In particular, Prescott demonstrated that sucralose can be used to estimate the likely wastewater impact in selected watersheds. The results also indicated that sucralose can be used to determine the vulnerability of a drinking water utility to wastewater-derived nitrosamine precursors: indeed NDMA presence is directly correlated to the amount of sucralose (and thus, consequently, of wastewater) present in a watershed. The greater the amount of sucralose detected, the higher the NDMA formation potential.

Taken together, all the evidences provided highlight that the strategy to decrease NDMA levels, and even prevent the formation of this possible carcinogenic molecule into the water, should be.

to avoid the use of NDMA precursors in water treatment processes. For this reason, many researches are currently focused on the identification of these precursors or the strategies and to remove them from water

3.5 Conclusions

The purpose of this section was to present a brief detailed explanation on monochloramine chemistry and biocide efficiency with particular attention to the formation of disinfection by-products (DBPs). There is always a lack of information or at least a poor scientific background when monochloramine is directly accused of being a chemical precursor for NDMA formation.

Monochloramine is produced by two different chemical reagents, a chlorine based solution and an ammonium salt. It is a great biocide with better features with respect to traditional chlorine based disinfection techniques and NH_2Cl produces less DBPs during the disinfection process.

Both the formation process and the biocidal action of monochloramine do not involve the formation of NDMA in the reaction paths. If a few chemical rules (the ones related to pH, reagent ratios, and monochloramine concentration) are respected, there is no chance for NDMA formation issues to occur.

The presence of NDMA in chloramination processes is due to two main causes. The first one is the presence of organic molecules that act as NDMA precursors. These molecules are more abundant in surface waters due to the presence of animals like birds and fish. The second reason is that, during an improper generation of monochloramine, where the reagents are not properly balanced, the formation of dichloramine can occur. These molecules can further react and convert other precursors into NDMA.

Therefore, the main focus to decrease the NDMA levels and prevent the formation of this possible carcinogenic molecule into water should be to avoid the use of NDMA precursors in water treatment processes. For this reason there is much research currently being done on how to identify these precursors and how to remove them from water.

4

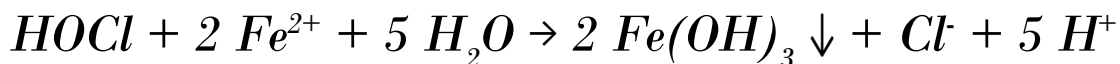
Chlorine, chlorine dioxide and monochloramine: what about corrosion?

4.1 Corrosion Concerns

When using disinfectants that base their mechanism of action on oxidation, corrosion is one of the most frequent and serious unintended concern to deal with.

As extensively described in the other Sections of this document, chlorine is a strong oxidant and thus can attack pipe materials (both metals and plastic) causing corrosion issues.

The reaction between chlorine and iron pipe is depicted below:



Reaction 7: iron (II) oxidation by chlorine

Boffardi (Boffardi et al., 1992) showed that at concentrations above 0.5 ppm chlorine leads to iron corrosion in drinking water piping. Several scientific and technical papers supporting this evidence can be easily found in the published literature and on the Internet.

More recently, it has been shown (Hassinen et al., 2004; Castagnetti et al., 2010) that chlorine is also corrosive on PE (polyethylene) and PP (polypropylene) pipes which are going to be more and more common for water distribution piping (particularly in Europe).

Chlorine dioxide is also reported to be corrosive both on metallic and plastic pipes (Yu et al., 2011, 2013) and it has been shown that corrosion reactions are the principal factor responsible for chlorine dioxide consumption in building water systems (Zhang et al., 2008).

Obviously, there is more and more concern for the corrosion of water pipes, especially considering the capital and operation costs required to fix it. Moreover, being iron a microelement that can improve *Legionella* metabolism, there are evidences suggesting that corrosion products enhance *Legionella* colonization in building piping systems. Eventually, the remediation of these premises piping systems becomes increasingly difficult due to the presence of such corrosion products.

By contrast, monochloramine has proven to be less aggressive than chlorine or chlorine dioxide towards pipe materials commonly used into building water system (Treweek et al. 1985; Le Chevallier et al. 1993; McNeill et al. 2001). Tests extensively carried out by our laboratories on different pipe materials (copper, galvanizer iron, stainless steel, PEX, PPR, C-PVC, unpublished results 2005 - 2015) show that this is actually the case.

The concern about elastomers is also taken into consideration: the first report stating that an oxidative attack on certain type of elastomers by monochloramine is possible was published by NACE (National Association of Corrosion Engineers) in 1961⁵. The most authoritative publication on compatibility between monochloramine and elastomers (namely NBR, EPDM,

⁵ National Association of Corrosion Engineers, 1961, Technical committee report rubber lining - resistance to corrosion. NACE Report Publication No. 61-13.

PTFE...) is the AWWARF book "Chloramine effects on distribution system materials" (Reiber, 1993): In this book cases of elastomer failure are reported and a possible failure mechanism (the attack on the sulfur cross-linkage of rubber) is proposed.

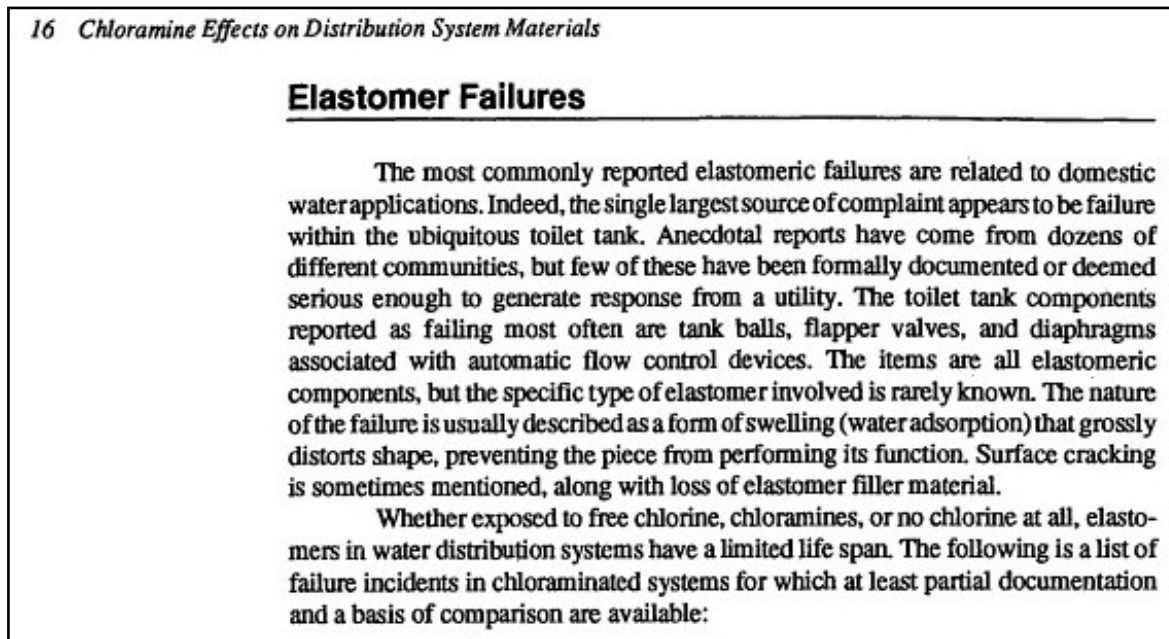


Figure 21: extract from the book "Chloramine effects on distribution system materials", AWWARF, 1993

The authors have more than 10 years direct experience with more than 700 applications in any type of premise showed that only old NBR (natural rubber) seals, gaskets or O-rings can be possibly attacked and swelled by monochloramine at drinking water levels (up to 4 mg/l) and that EPDM is much more resistant, even in hot water. Of course, fluorinated polymers like PTFE, PVDF, PFA,... are completely resistant to both monochloramine and chlorine even at higher temperatures and pressures.

However, some concerns still remain about monochloramine induced corrosion, especially with copper pipes. This problem is related to one monochloramine by-product: ammonium ion (NH_4^+). This cation is in equilibrium with its not-protonated form, ammonia (NH_3). This equilibrium is pH dependent: higher pH values favor ammonia formation and vice versa. Both molecules are often referred as "free ammonia". These concerns come from the fact that ammonia could form soluble copper-ammonia coordination complexes. Free ammonia formation is influenced by several different factors, but mainly by water temperature and water age. Pipe systems with high temperatures in the heat exchangers and low water consumption (high water age) are more likely where free ammonia could be found. This is true regardless of whether monochloramine is applied as a supplemental disinfectant and/or comes directly from the municipality water.

When in contact with most drinking water supplies, copper develops a protective layer of copper oxides and copper carbonates on the internal surface of the pipe. This phenomenon

is known as passivation. However, even if the protective layer is present, there can be small areas in which there are some irregularities on the layer. In those spots corrosion may occur. Chlorides initiate the corrosion process and it has been demonstrated that the first product of copper corrosion in all the types of water is copper (II) hydroxide $[\text{Cu}(\text{OH})_2]$ (Edwards et al., 1996). Other factors that can facilitate the starting step and then favor the propagation of copper corrosion are pH, water temperature, dissolved oxygen, water alkalinity, carbonates and water linear velocity (Oliphant et al., 2003). In particular, it has been demonstrated that dissolved oxygen increases the corrosion rate at concentrations up to 4 ppm. Free ammonia is not listed in the factors that starts or propagates the copper corrosion, therefore is not corrosive towards copper at drinking water ranges.

A published work carried out by Hoar and Rothwell (Hoar et al., 1970) reported the pH/potential diagrams of copper with water/ammoniacal solutions: they described the possible interactions among copper oxides (CuO and Cu_2O) and either ammonia or ammonium ion to generate copper-ammonium complexes. However, all the tests were carried out with a concentration of free ammonia ($\text{NH}_4^+ + \text{NH}_3$) that was much higher than drinking water range. Concentrations in the study were in the order of grams per liter (10,000 ppm) while drinking water range concentrations of free ammonia are in the order of tenths of milligrams per liter (< 0.5 ppm).

Free ammonia is not a regulated disinfection by-product under the EPA Safe Drinking Water Act (SDWA). In general, monochloramine does not generate any regulated DBPs. The suggested free ammonia limit at 0.5 ppm has been identified as a safe threshold that is way below the concentration that can cause problem related to corrosion. The SANIKILL patented system developed by the Authors limits the formation of free ammonia in the water in order to keep free ammonia levels well below 0.5 ppm. With free ammonia concentrations in the order of tenths of ppm, its effect on copper corrosion is nil.

Sanipur has participated in several third party validated research studies with different Universities and Research Centers to confirm the efficacy of the system and to evaluate any possible corrosion issues. Corrosion was not identified on copper pipes in tests carried out both at low temperatures ($20^\circ\text{C} - 25^\circ\text{C}$, $68^\circ\text{F} - 77^\circ\text{F}$) and high temperatures ($50^\circ\text{C} - 55^\circ\text{C}$, $120^\circ\text{F} - 130^\circ\text{F}$) with monochloramine concentrations within drinking water range ($2 - 3$ ppm). Additionally, different studies aiming at evaluating the corrosion effect of different disinfectants on copper and other metals have also been published in the peer reviewed literature. In particular, Rahman (Rahman et al., 2007) carried out several experimental tests using chlorine dioxide, free chlorine and monochloramine at different concentrations (all concentrations within maximum regulated disinfectant level under the Safe Drinking Water Act) to analyze the corrosion effect of the biocides at different contact times. In all the tests, monochloramine showed total copper residuals no higher than 0.60 ppm for almost the whole study, except for the beginning, when total copper residuals have been detected at around ≈ 0.80 ppm.

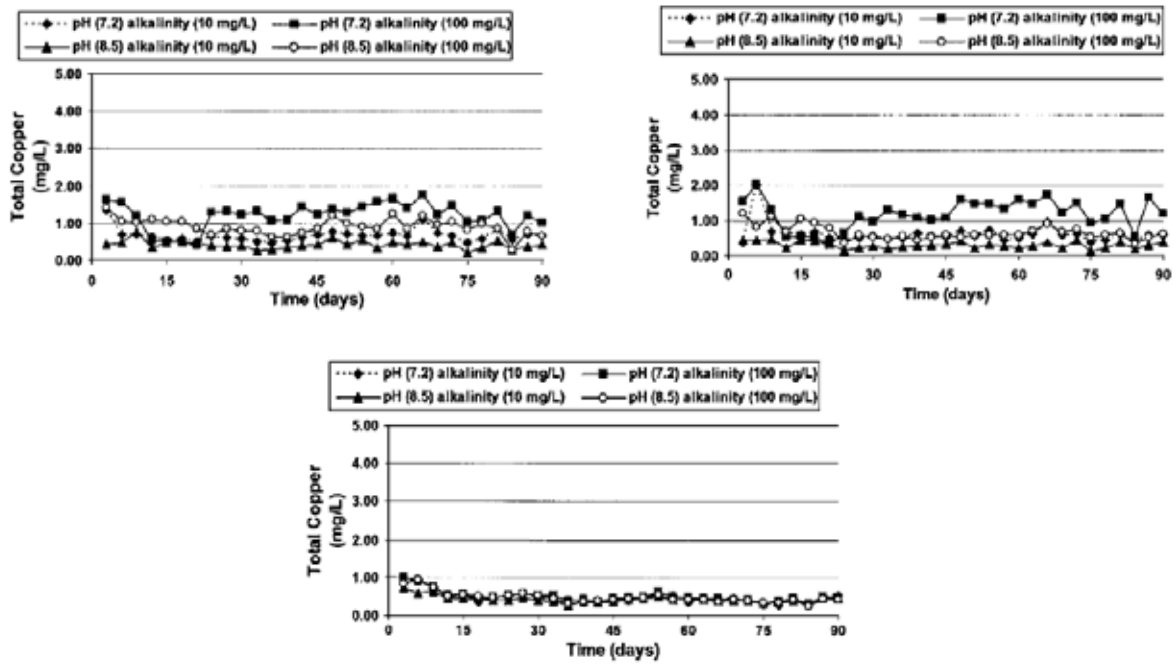


Figure 22: Total copper release (ppm) measured in different experimental condition with chlorine dioxide (A), free chlorine (B) and monochloramine (C) (Rahman, 2007).

In another study, Zhang (Zhang et al., 2002) calculated that copper corrosion rate in presence of monochloramine at drinking water range (maximum 4.00 ppm) is in the order of just 0.1 $\mu\text{m}/\text{year}$. Another comparison between the corrosion effect of disinfectants (monochloramine and chlorine dioxide on carbon steel C1010 in this case) is reported in the study published by Marchesi (Marchesi et al., 2016). The carbon steel coupons were installed into sample racks piped in the return line to the water heater of a hospital for six months. One rack was installed into a wing treated with monochloramine while the other one was installed into a different domestic hot water loop treated with chlorine dioxide. The loss in the thickness of the coupons over the six months period never exceeded the average value of 0.50 millimeters/year (which is consider a satisfactory value) for all the coupons treated. However, the sample treated with chlorine dioxide showed the formation of localized pitting corrosion whereas the coupons exposed to to monochloramine didn't shown the presence of any pit on their surfaces.

4.2 Conclusions

Corrosion is one of the biggest concerns when a supplemental disinfection system is installed into a building. High corrosion rates result in high capital cost to replace pipes and other building water system equipment.

The corrosion rates are influenced by several different factors and the type of disinfectant is one of them.

Thanks to its lower oxidation potential and its stability, monochloramine has demonstrated to be far less aggressive than traditional chlorine and chlorine dioxide towards all pipe materials. Scientific studies demonstrated that chlorine and chlorine dioxide are extremely aggressive on pipes at concentrations that are as low as 0.50 ppm and 1.00 ppm respectively. Monochloramine instead, barely influences pipes at concentrations of 2.00 ppm.

Monochloramine does not directly react with metals, but free ammonia (a monochloramine potential by-product) could increase the metal release rates especially with copper plumbing systems. The key is then to have a system that is capable to control and diminish the ammonia formation rates when monochloramine is used as a supplemental disinfectant.

5

Do not underestimate the Regulation

5.1 Europe: The Biocidal Products Regulation

What is a biocide? In the European legislation, a biocide is defined as a chemical substance intended to destroy, deter, render harmless, or exert a controlling effect on any harmful organism. Thus, a disinfectant dosed into any kind of water with the aim of preventing the proliferation of microorganisms that can potentially represent a risk for human health is classified as biocide.

In order to harmonise the market of such products at Union level, the EU issued the Biocidal Products Regulation (BPR, Regulation (EU) 528/2012): it came into force on September 1st 2013, replacing the European Biocidal Products Directive 98/8/EC (BPD), and is now law in every European Member State. This regulation aims not only at improving the functioning of the biocidal products market in the EU but also at ensuring a high level of protection for both humans and the environment.

This regulation should also allow to simplify the approval of active substances (i.e. the ingredients responsible for the biocidal activity) and the authorisation of biocidal products.

According to the BPR, before any biocide being placed on the market, the manufacturers and suppliers must first get the active substance approval at Union level. Then, the biocidal product itself have to be authorize at Member State level, or, alternatively, at Union level (Union authorisation).

It is important to point out that biocides are classified in 22 different product types (PTs), according to their intended use: as an example, within the “macrocategory” of disinfectants, the biocidal products used for drinking water disinfection are classified as PT5. Each active substance or biocidal product is not evaluated per se, but as referred to one or more specific product types.

According to Art. 95 of the BPR, as of September 1st 2015, a biocidal product consisting of, containing, or generating a relevant substance, cannot be made available on the EU market unless the substance supplier or product supplier is included in the list for the product type(s) to which the product belongs. To be included in the “Article 95 list”, available from the European Chemicals Agency (ECHA) website (<https://echa.europa.eu/it/information-on-chemicals/active-substance-suppliers>), a company have to submit its own dossier or a permit to access documentation for active substances submitted from other applicants.

What about monochloramine? As described in the previous section, monochloramine must be generated in situ from chlorine and ammonia sources.

Being an in situ generated active substance, monochloramine can fall within the scenarios considered by Article 93 of the BPR, that outlines transitional provisions for biocides that weren't regulated under the BPD but are now regulated under the BPR. For these products, only the companies that have submitted applications for approval of the specific “precursors - active substance - PT” combinations by September 1st 2016 can take advantage of a transition period:

indeed, if an appropriate application had been made according to the deadline, the applicants can continue to use and distribute their biocidal products until the end of the relative evaluation process.

Sanipur submitted its own Biocide Dossier for monochloramine to ECHA respecting the deadline of September 1st 2016. Thus, nowadays, Sanipur - founding partner of the “European Monochloramine Cooperation” - is one of the only two European companies (and the only one in Italy) listed on the “Art. 95 list” for the use of monochloramine for drinking water disinfection (BPR - PT5).

5.2 U.S. and Canadian Certification:

NSF/ANSI/CAN 61

Sanipur is the only company who has all its monochloramine generators models certified to NSF/ANSI/CAN Standard 61.

NSF/ANSI/CAN Standard 61 was developed to establish stringent requirements for the control of potential adverse human health effects from products that contact drinking water, as supplemental water disinfection units.

Certification to NSF/ANSI/CAN Standard 61 ensures that the SANIKILL monochloramine generators meet the regulatory requirements for the U.S. and Canada, and it can often meet or fulfill the testing requirements for many other countries as well. This marks ensures all our customers that the SANIKILL monochloramine generators don't leach or produce harmful contaminants into drinking water during regular operations.

The NSF mark is also well respected by public health officials, drinking water utilities and it is recognized as a symbol of product quality and integrity.

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