Sanipur

Monochloramine for Building Water System disinfection.

The science behind.

Summary

Disclaimer

The author is affiliated to Sanipur US LLC, which are selling disinfection technologies based on chlorine, chlorine dioxide and monochloramine for Legionella remediation. This white paper is a scientific report that, in its purpose, would like to be unbiased by the commercial activity of Sanipur US LLC.

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"The Iron Fist in the Velvet Glove."

1. Understanding chlorine chemistry:

the beauty of the electron clouds

US-EPA listed disinfectants for drinking water are all based on the Cl atom[1]. The efficacy of these disinfectants against Legionella vary significantly as shown in the picture below:
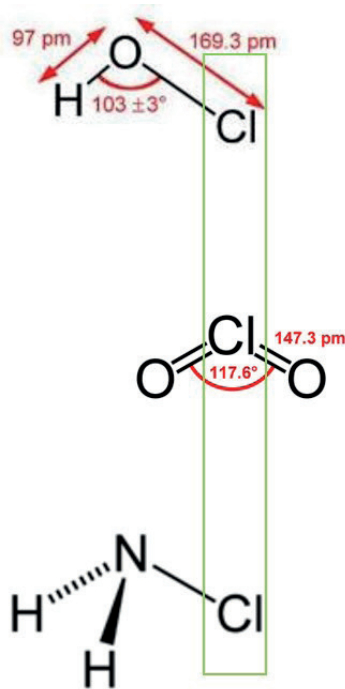
Chlorine/Hypochlorous acid-hypochlorite is the less effective among Cl-based disinfectants and at least 2-3 ppm are needed to reach a fair remediation. Under these conditions chlorine is highly corrosive against both metallic and plastic piping. Its effect is strongly pH-dependent and regulated toxic by-products (THM) 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 where it 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 one can see from 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".

Why, then is the first an acid and the second acts more like a base? This is because of the different behavior of their partner atom. Figure 5 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.

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[1] http://water.epa.gov/drink/contaminants/basicinformation/disinfectants.cfm

Nitrogen is a soft atom (the red cloud is spread all over the bond between Cl and N) and the molecule it generates – monochloramine, NH2Cl – is less oxidant compared to those of oxygen: chlorine is less prone to break the bond with nitrogen since this one tends to shares its electrons with the partner atoms.
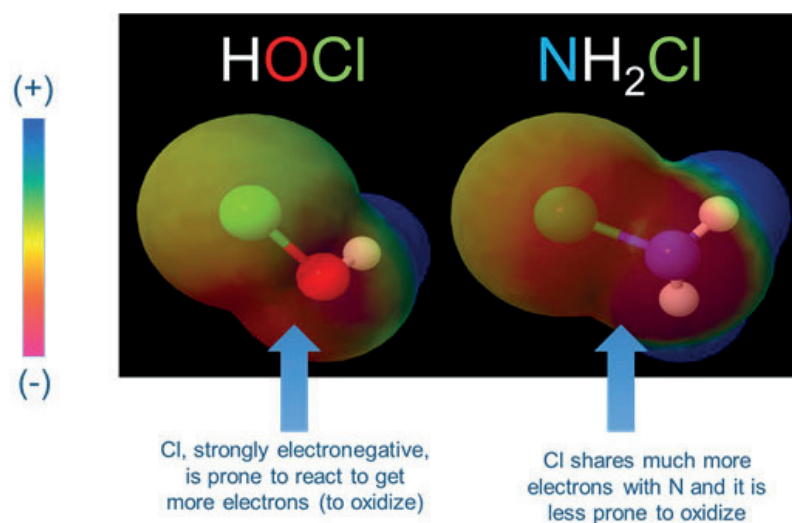
Figure 2: Van der Waals surfaces (representing electron density) of HClO and NH$_2$Cl. Modeling and calculations are made by the author with MolView v2.1.3

This is the main reason for the different chemical behavior of these molecules.

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:

$$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O$$

Reaction 1: monochloramine generation from ammonia and hypochlorous acid

As represented in Figure 2 chlorine abandons oxygen for a new electron-donor partner.

During this reaction, other chloramines can form (di and tri chloramines, respectively NHCl2 and NCl3) and pH plays a key role in the selection of the desired product.

The following figures demonstrate the effects of pH on chlorine and chloramine chemistry. Drinking water pH ranges favors monochloramine.

The following picture shows the effect of pH on the relative concentration of these three molecules:
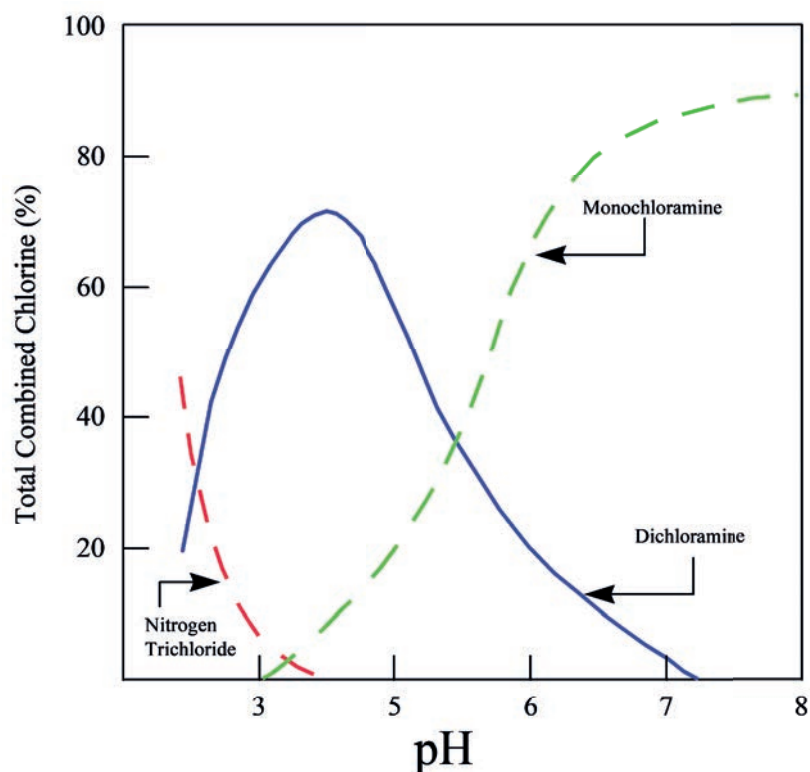
Figure 3: chloramines species as a function of pH. Source: Palin, A. 1950. "A Study of the Chloro Derivatives of Ammonia." Water and Water Engineering. 54:248-258

Monochloramine is very stable and the predominant species at pH above 7.2. At this pH 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 toxic and odorous molecules. Trichloramine moreover is an explosive liquid but fortunately, it cannot form in the normal drinking water matrix.

The following picture shows the forms in which chlorine can be present at different pH. As one can see 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.

$$HOCl \leftrightarrow OCl^- + H^+$$
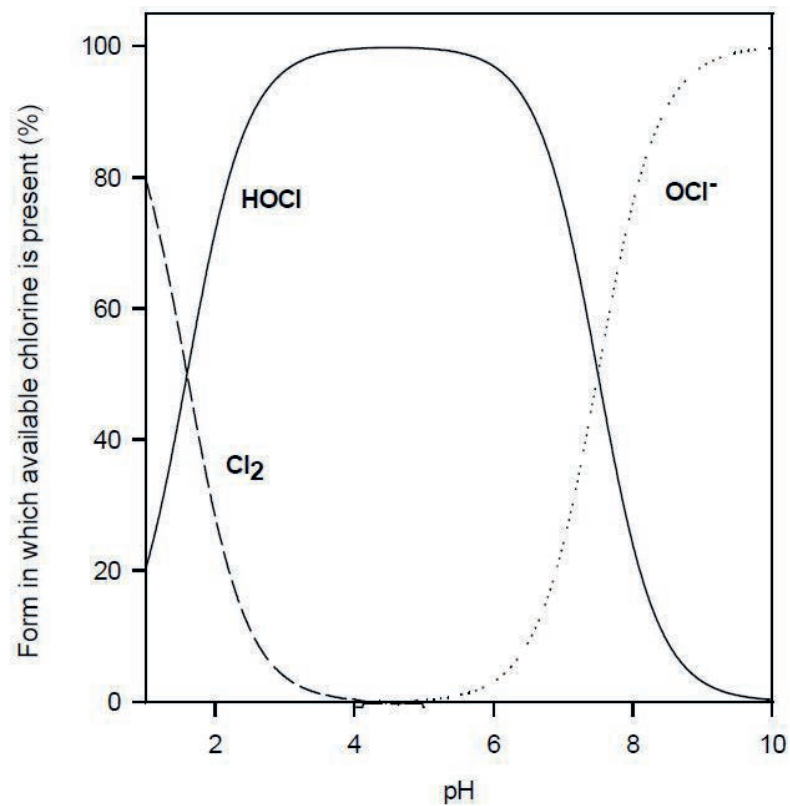
Figure 4: different free chlorine species present as a function of pH

The comparison between the figures 3 and 4 clearly shows that in the pH range of drinking water the monochloramine is present 100% in its active form while hypochlorous acid is present in a mixture with hypochlorite ion and that the percent of the active form of free chlorine 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 explain 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. This same pH of 8.0 is ideal for formation of monochloramine leading to high biocidal efficacy and much lower corrosivity. Working like 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.

This is an important issue, since when one add chlorine to water he has to account for the non-biologically active but highly oxidant (corrosive) part of it. And this part increases with the pH.
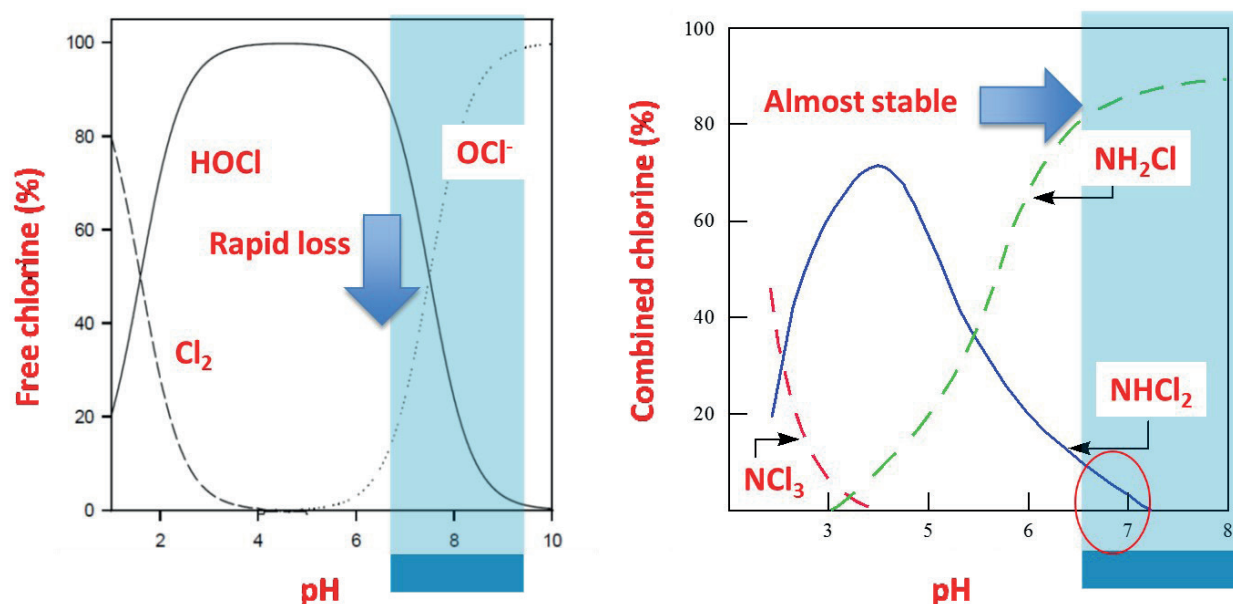
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For example, in order to have 1ppm of active free chlorine (HClO) at pH 8, one should add 5 ppm of chlorine, since only the 80% of it dissociates into hypochlorite ions (OCl⁻). Whereas, in order to have 1ppm of monochloramine one just adds 1 ppm of chloramine: *no wasted chemicals, no corrosion issue, less by-products.*

Chlorine dioxide behaves differently from the other two Cl-based biocides: chlorine and mono-chloramine. First of all it is a dissolved gas and not a molecule in solution, it is also a radical, thus very reactive.
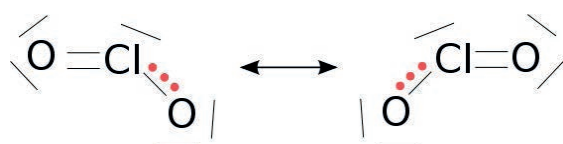
Reaction 2: resonance structures of chlorine dioxide

Its chemistry is very complex and fascinating. Its reactivity is not very much influenced by pH in the drinking water pH range. Having an unpaired electron (see Reaction 2 Reaction 1) this molecule is very reactive, thus it has low CT values[2] but also it is highly corrosive. Its nature as a gas in solution 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 leaks. This will be discussed in the pertinent section of this paper.

CT values of monochloramine are higher than that for chlorine and chlorine dioxide. This is due to the lower oxidation potential of this disinfectant. This is not a drawback, however, because the stability and low reactivity of monochloramine helps it to better penetrate biofilms and kill bacteria inside it. This is 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 is achieved. *This feature is very useful to keep out contamination in dead legs during commissioning and renovation*. Monochloramine stability helps this biocide remain stable and effective at the proper concentration in low flow regimes (oversized pipes, temporary dead legs, varying flow situations) where other biocides fail.

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

[2] CT values are 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 microorgamisms 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]

2. Biofilm penetration: monochloramine does it better

The following picture shows the different penetration profiles of biofilm for chlorine/hypochlorous acid and monochloramine, as recently reported in the scientific literature (Lee 2011).
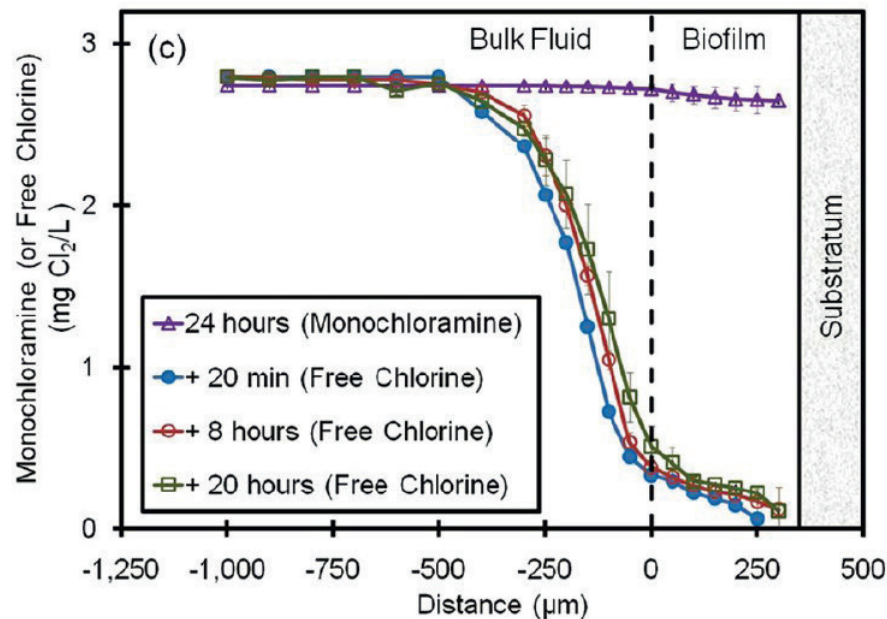
Figure 6: biofilm penetration of free chlorine and monochloramine determined by microelectrodes (Lee 2011).

Monochloramine and free chlorine have similar diffusion velocities in water at 77°F (25°C), so they reach the biofilm the same way. When they reach the biofilm they can react with the biological material (exopolymeric substances, EPS) excreted by microorganisms and are consumed or they can continue the diffusion process. The measured free chlorine microprofiles shown in the picture detail the differences in behavior between free chlorine and monochloramine with biofilm constituents. Whereas chlorine promptly reacts with EPS and is consumed, monochloramine diffuses in the biofilm without being consumed. Free chlorine reacts faster with EPS and the external biofilm layers and it is consumed before it can reach the inner regions of the biofilm where most of the Legionella bacteria lurk. *This is the first published demonstration of the superior ability of the monochloramine to penetrate biofilms.*

There is only one publication (Jang 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. Concentrations are higher than those typically encountered in drinking water application (0.2 – 0.8 mg/l) but it is impressive to note the penetration profile of this molecule is similar to that of chlorine.
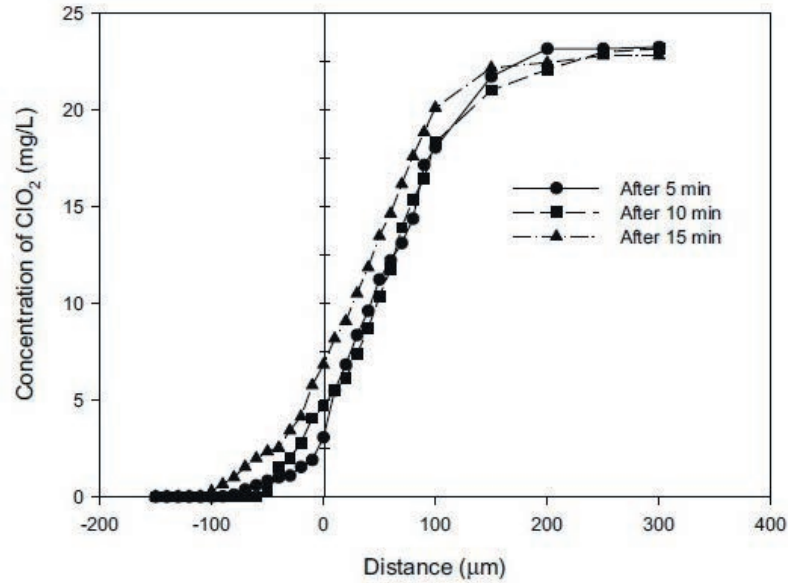
Figure 7: biofilm penetration of free chlorine dioxide determined by microelectrodes (Jang 2006).

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

Higher biofilm penetration means no wasted chemicals. In order to achieve the same biofilm penetration chlorine or chlorine dioxide must be added in higher concentration since it is consumed by the external biofilm layers. Higher chemical dosed, much of it wasted, means higher costs of treatment. It should also be remembered that, in the case of chlorine, at the usual drinking water pH only a fraction of chlorine is active free chlorine, the remaining part of it is not just waste, it is a strong oxidizer (hypochlorite ion) added to piped water. This strong oxidizer is responsible for the high metal corrosion rate of the chlorinated water compared to the chloraminated water.

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3. Unintended consequences of disinfection: no surprises if you know chemistry

There are some publications dealing with unintended consequences of incorrect or uncontrolled monochloramination of drinking water [Symons 1998, Mitch 2003, Edwards, 2005]. These publications are very useful since they point out the consequences of an improper monochloramine generation technology. 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, HAA, organic chloramines. NDMA can be generated by either chlorine or monochloramine. A recent study pointed to the fact that this NDMA is statistically generated, under particular circumstances, by monochloramine at a higher rate [Woods and Dickenson 2015]. The authors experience with monochloramine shows that it is very unlikely the NDMA forms under the proper method of generation and control of monochloramine (Garusi 2009). A new publication by an independent research group on this subject is schedule for publication in 2016.

The facts is, chlorine generates much more (regulated) toxic DBPs than monochloramine and this is why many larges municipalities in the US have moved to monochloramine to comply with the DDBPR Stage 2[3] regulation. Chlorine by-products are well known and regulated all over the world. The regulation is focused to THMs, but also includes chlorite and chlorate, haloacetic acids (HAAA5), chlorinated organic molecules, bromide and bromate. Being stronger oxidant chlorine undergoes more redox reactions compared to monochloramine.

Chlorine dioxides 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 MCL (0.8mg/l)[4] for chlorite.

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

In order to obtain the right environment in the monochloramine generation, as depicted in Reaction 1, the physical and chemical parameters must be controlled (Scheiber 2005). Now on the market the technology to do that is available and mature.

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[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

The only theoretical by-product of the monochloramine generation (Reaction 1) is water(!) but, due to the fact that the real yield is lower than 100% you can expect a small amount of free chlorine and free ammonia as the main side products if the pH is properly controlled (pH > 7.2 in the reaction chamber).Other side reactions that can occur are the formation of di- and tri-chloramine but they are favored at low pH (see Figure 5), uncommon in drinking water. The chemical composition of the reagents and the reaction chamber can be engineered so that the optimal conditions for the formation of monochloramine are realized.

THM's can be also produced in the chloramination process by the reaction between free chlorine (hypochlorite) and natural organic matter (NOM) like in a standard chlorination process, but the formation of these by-product can be minimized by the proper reagent addition order of addition as already stated above (Scheiber 2005). 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.

The main by-product of the monochloramination reaction in drinking and domestic hot water loops is the ammonium ion (NH_4^+) produced by the decomposition of monochloramine when the water consumption is low or negligible, for example overnight (see Figure 8).
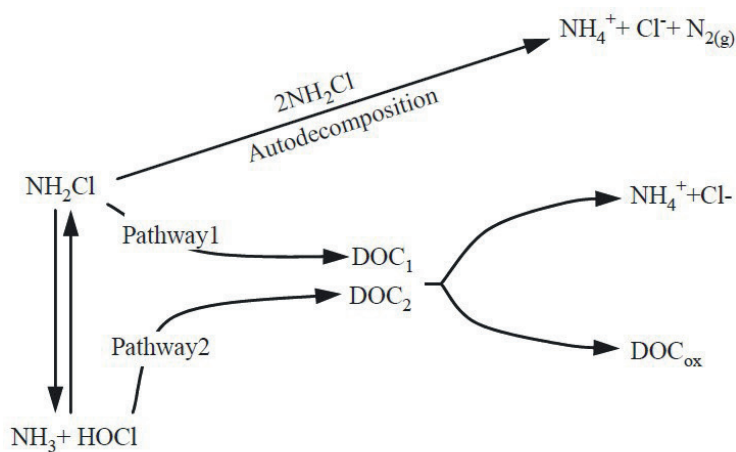
Figure 8: schematic of monochloramine reaction pathways in the presence of NOM. DOCox represents oxidized NOM (Duirk 2005)

Thus, the control of the ammonium ion is mandatory to avoid potential nitrification and corrosion of copper piping (via the stable $Cu(NH_3)_6^{2+}$ coordination complex). The technology to do that is now available and ammonia residuals as low as < 0.2ppm are not uncommon in properly controlled chloraminated water.

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

Corrosion of metal and plastic pipes with chlorine, chlorine dioxide and mo-nochloramine: the true story.

Chlorine is a strong oxidant and can attack pipe materials (both metals and plastic) to provoke corrosion issues.

The reaction between chlorine and iron pipe is depicted below:

$$HOCl + 2\ Fe^{2+} + 5\ H_2O \rightarrow 2\ Fe(OH)_3 \downarrow + Cl^- + 5\ H^+$$
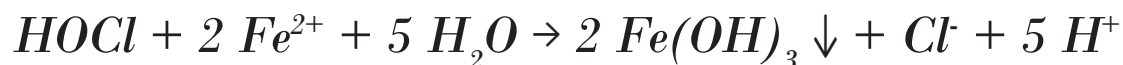
Reaction 3: iron (II) oxidation by chlorine

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

More recently, it has also been shown (Hassinen 2004, Castagnetti 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 on plastic pipes (Yu 2011, 2013) and it has been shown that corrosion reaction are the principal factor responsible for chlorine dioxide consumption in building water systems (Zhang 2008).

There are more and more concern over the corrosion of water pipes do to the capital and operation cost needed to fix it. Moreover, iron being a microelement improving Legionella metabolism, there are evidences that corrosion products enhances the Legionella colonization in building piping systems. Eventually, the remediation of these premises piping systems becomes increasingly difficult due to the presence of the corrosion products.

Monochloramine instead is shown to be less aggressive towards pipe materials (Treweek 1985, Le Chevalier 1993, McNeill 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 in this paper.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 1961[5]. The most autho-

[5] National Association of Corroison Engineers, 1961, Technical committee report: rubber lining – resistance to corrosion. NACE Report Pubblication No. 61-13.

ritative paper on compatibility between monochloramine and elastomers (namely NBR, EPDM, PTFE…) is the AWWARF book titled "Chloramine effects on distribution system materials" (Reiber 1993). In this book the author reports cases of elastomer failure and a possible failure mechanism (attack on the sulfur cross-linkage of rubber).

16 Chloramine Effects on Distribution System Materials

Elastomer Failures

The most commonly reported elastomeric failures are related to domestic water applications. Indeed, the single largest source of complaint appears to be failure within the ubiquitous toilet tank. Anecdotal reports have come from dozens of different communities, but few of these have been formally documented or deemed serious enough to generate response from a utility. The toilet tank components reported as failing most often are tank balls, flapper valves, and diaphragms associated with automatic flow control devices. The items are all elastomeric components, but the specific type of elastomer involved is rarely known. The nature of the failure is usually described as a form of swelling (water adsorption) that grossly distorts shape, preventing the piece from performing its function. Surface cracking is sometimes mentioned, along with loss of elastomer filler material.

Whether exposed to free chlorine, chloramines, or no chlorine at all, elastomers in water distribution systems have a limited life span. The following is a list of failure incidents in chloraminated systems for which at least partial documentation and a basis of comparison are available:

Figure 9: extract from the book "Chloramine effects on distribution system materials", AWWARF, 1993

The authors 10 years direct experience with more than 200 applications in any type of premise showed that only old NBR (natural rubber) seals, gasketsor 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, PFVD, PFA,… are completely resistant to both monochloramine and chlorine even at higher temperature and pressure.

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4. The volatility issue

Chlorine dioxide, being a gas in solution, has the highest volatility. Hypochlorous acid and mo-nochloramine are nonetheless volatile compounds (Holzvarth 1984). Hypochlorite, being an ion in solution is not. Thus, since hypochlorite and hypochlorous acid are present simultaneously in drinking water (see Figure 4) and the fraction of hypochlorous acid depends on pH, the volatili-ty 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 this is not the case for 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 evaporates an equilibrium is established and the process stops). Moreover, being monochloramine is far less aggressive than chlorine, the risk corrosion of wetted and air exposed components is greatly reduced.

Authors	Disinfection method	Concentration	Result
Helms CM, JAMA 1988	Chlorine	3-5 mg/l	From 29% to <5% positive sites after 5 years
Snyder MB, J Infect Dis 1990	Chlorine	2 -5mg/l	From 37% to 7% positive sites after 17 months
Ditommaso S, Infect Control Hosp Epidemiol 2006	Chlorine	2-3 mg/l	From 47% to 6% positive sites after 5 years
Hamilton E, J Hosp Infect 1996	Chlorine dioxide	0.5–1 mg/l	From 28% to 12% positive sites after 6 months
Srinivasan A, Infect Control Hosp Epidemiol 2003	Chlorine dioxide	0.8 mg/l	From 41% to 4% positive sites after 17 months
Scaturro M, Infect Control Hosp Epidemiol 2007	Chlorine dioxide	0.4–0.5mg/ l	Persistent colonization of water system
Casini B, J Hosp Infect 2008	Chlorine dioxide	0.2–0.5mg/ l	From 67% to 14% positive sites after 5 years
Hosein IK, J Hosp Infect 2005	Chlorine dioxide	0.5 mg/l	From 40% to 50% positive sites after 2 years
Zhang Z, Infect Control Hosp Epidemiol 2007	Chlorine dioxide	0.5–0.7mg/l	From 60% to 10% positive sites after 30 months
Sidari F, AWWA Journal 2004	Chlorine dioxide	0.3 – 0.5 mg/l	From 27% to 3% positive sites in 1 month
Di Marino O, EWGLI2007	Chlorine dioxide	0.2 – 0.3 mg/l	From 60% to < 5% in 1 month
Borella P. et al., AJIC, 2012	Monochloramine	2-3 mg/l	From 60% to 8% positive sites in 1 month
Kandiah S, 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., Infectous disorders, 2013	Monochloramine	2-4mg/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

5. Efficacy of monochloramine for Legionella remediation compared to chlorine and chlorine dioxide

In the following table, selected scientific literature is reported that show the different efficacy of the three Cl-based biocides and to support the statements reported in Figure 1.

Chlorine, as stated in Table 1, is the least effective chemical in remediating Legionella. This is due to the drawbacks extensively discussed in this paper which are inherent to the chemical behavior of these molecules: hypochlorous acid/hypochlorite ion that represent the real nature of chlorine in aqueous media.

Accordingly, chlorine, despite its low cost as a chemical, suffers high use costs for remediation due to its pH-dependency (active chlorine concentration is low at drinking water pH), corrosivity (Hassinen 2004, Castagnetti 2011) and stability (being highly reactive it is not stable in hot water). Moreover, recent publications put forward the risk of a potential resistance of legionella biofilms to chlorination (Cooper 2010, Bodet 2012).

Chlorine dioxide could be a better choice compared to chlorine (remediation results are better) although it suffers several drawbacks, described here above, that limit its application. First of all it is a gas in solution and a hazardous chemical. For drinking water application, it is principally produced by mixing sodium chlorite and hydrochloric acid. Chlorine dioxide is a potential explosive gas thus 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 are reported in a preceding section.

Conversely, the literature survey reported in Table 1 clearly reports that the best remediation results have been obtained by application of the monochloramine, mainly in hot water only (see next section for the reason for this choice). As shown earlier, this efficacy is the result of some monochloramine most beneficial properties (electron sharing, stability, pH and ORP functions, biofilm penetration ability, decay pathways). A thorough knowledge of the monochloramine chemistry is thus needed to take advantage of these properties to obtain the desired remediation results. Monochloramines more widespread use and understanding has only occurred recently. This is possibly the main reason why it has taken some time for monochloramine to affirm itself as a superior biocide for secondary disinfection of building system.

In fact, only in the last 10-15 years has evidence that monochloramine could be a potential disinfectant for Legionella remediation started to be available in the scientific literature (Kool 2009, Gao 2000, Hellefinger 2003, Flannery 2005). In 2005 Loret (Loret 2005) and McCoy (McCoy 2005) supported the effectiveness of monochloramine by scientific data and envisages the need for a generator for this chemical, which was not yet available on the market at that time. The difficulties in controlling the monochloramine generation and concentration into the water systems were the major obstacles that have been solved recently by a new patented technology (Garusi 2009). It was as recent as 2011 (Lin 2011 Kandiah 2012) when the first commercial application was investigated and reported in the United States.

The author contributed to the development of said commercial system and its efficacy is now supported by strong scientific evidences (Casini 2014, Duda 2014, Coniglio 2015a 2015b 2015c, Kandiah 2012 2013, Marchesi 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 2003).

6. Some like it hot

Among the scope of building water system disinfection there is Legionella remediation (ANSI/ASHRAE Standard 188-2015). Focusing on the place where Legionella bacteria colonize (domestic hot water systems) gives the remediation application the best chance to succeed and save lives and money.

There are essentially three reasons why disinfection of the hot water only for Legionella remediation is preferable:

i. Chemistry

Monochloramine produces less regulated disinfection by-products (DBPs') than chlorine or chlorine dioxide A few THMs' or other by-products can be produced depending on the water quality. Dosing monochloramine on domestic hot water eliminates the risk of increasing DBPs in the building drinking water system. This eliminates any potential problems of unnecessarily exposing building occupants to DBP's in cold drinking water.

ii. Microbiology

Legionella do no colonize well in cold water temperatures. Also, some authors reported that monochloramine on cold water modify the microbiological environment and gave rise to an increase of mycobacterium and coliforms populations upon conversion to monochloramine, but this is still controversial, since recent publication show a different situation in building hot water systems (Duda 2014). These have not been reported in the application of monochloramine on hot water if the residual is above 2 ppm (Duda 2014, Casini 2014, Borella 2013). Dosing monochloramine on hot water only reduces the risk of nitrification since nitrifying bacteria are less likely to colonize in hot water temperature environments. Regardless of the point of application the dosing system selected for monochloramine feed must be able to control free ammonia formation. This is the key to preventing nitrification and controlling increased corrosion of copper resulting from free ammonia.

iii. Economics

Again, Legionella bacteria do not colonize or populate in cold water environments. Domestic hot water consumption in a premise could be as low as one tenth (1/10) of total cold water consumption. In hundreds of applications in Europe and the US the authors experience in hospital environments has found domestic hot water use to be 6-10%fo total domestic water use. Therefore, proportional savings in reagents consumption and cost are experience when treating the hot water only. It should be understood that bacteria colonized in the plumbing fixture will be disinfected by the monochloramine in

the hot water only. Chlorine and chlorine dioxide are reported to decompose very quickly in hot water, thus they are not suitable substitutes of monochloramine also from the cost control point of view.

As already reported above, there are a significant number of publications dealing with successful Legionella remediation supplying monochloramine in hot water only (Casini 2014, Duda 2014, Coniglio 2015a 2015b 2015c, Kandiah 2012 2013, Marchesi 2011 2012 2013).

2

"Cold vs. Hot water Considerations"

1. Legionella in plumbing 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, temperature and the design of the plumbing system in the building. As relates to plumbing system design, it is extremely important to apply good engineering practices that minimize dead legs and section of the pipes with low flow linear velocity, the presence of tank type water heaters and consideration for selection on the piping materials.

However, even though the plumbing systems design and materials influence Legionella growth, the water temperature plays the key role in this unwanted process. It is repeatedly reported in the scientific literature that the optimum growth of this pathogen is found to be at T= 37 °C (≈ 99 F) (Wadowsky et al., 1988; Yee et al., 1982). For this reason, domestic hot water systems present a perfect environment for Legionella colonization.

The results reported in Table 1, show the incidence of the temperature and the pipe material on the total flora and specifically on Legionella pneumophila (Rogers et al., 1994).

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

Table 1: Effect of temperature and pipe material on the total flora ad L. pneumophila colonization [4].

As shown in the experimental results reported in Table 1, temperature has a deep impact on Legionella growth; in fact, the number related to L. pneumophila is ≈ 30 times higher switching from 20 °C to 40 °C with PVCs pipes and ≈ 168 times with polybutylene pipes for the same temperature range.

Even though the literature reports that at temperatures around ≈ 50 °C the pathogen starts to decrease, it does not mean that that temperature completely reduce the risk of Legionella. In fact, some of the bacteria can survive when protected by the biofilm (Dennis et al., 1984).

Moreover, as reported in Figure 1, when temperature close to 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.
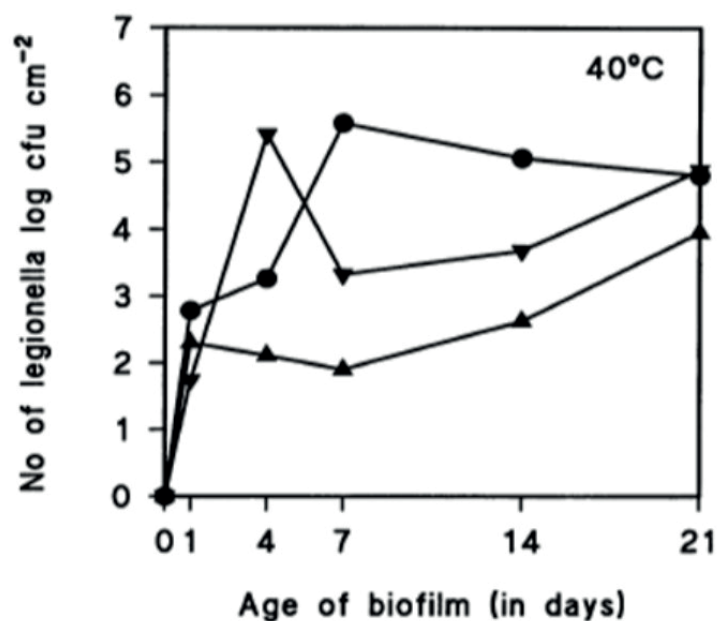

Figure 1: growth of Legionella pneumophila measured experimentally at T=40 °C and with different pipe materials. Circle: Polybutylene; Up-Triangle: Copper; Down-Triangle: PVCs (Rogers et al., 1994).

This strong relation between Legionella and the system temperature has linked the occurrence of this waterborne pathogen with warm water system in around the 85 % of the cases where Legionella was found (Ruf et al., 1988).

2. Secondary disinfection remediation treatments

The municipality water treatment plants usually use chlorine as the first disinfectant to kill the bacteria and chlorine or monochloramine as secondary disinfectant. The second step disinfectant aim is to keep a residual of biocide in the water which goes from the treatment plant into the building in order to avoid the growth of bacteria. However, a biocide is an oxidizing agent, and even though it could be more or less stable, sometime its decay rate can lead to a very poor disinfectant residual in the water that is approaching the buildings.

Since the risk of Legionellosis is directly related to the presence of this bacteria in the water system, healthcare facilities (hospital, nursing homes), Hospitality (hotels, casinos) and condominium complexes are more and more concerned about this threat. For this reason, the installation of on-site (supplemental) disinfection treatment units has become more widespread in recent years in order to kill the bacteria that survive the first two steps of municipal disinfection EPA listed disinfectants used as primary and secondary disinfectants are ozone O_3, chlorine (HClO), chlorine dioxide (ClO_2) and monochloramine (NH_2Cl).
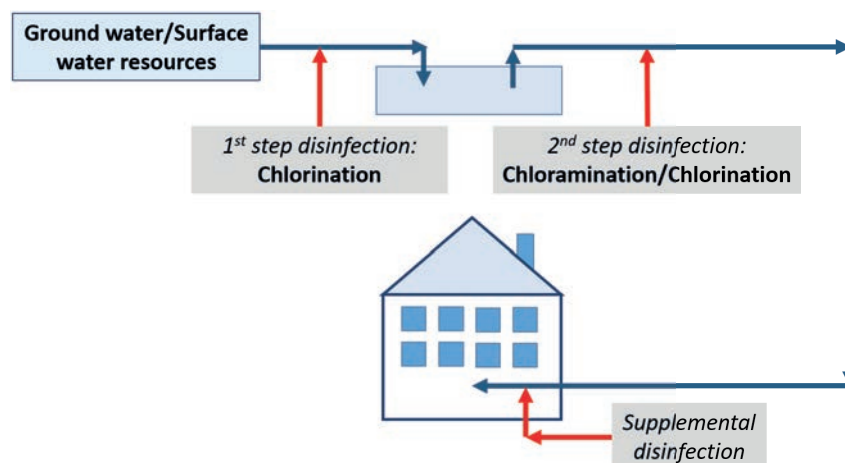

Figure 2: Typical scheme from municipality treatment plants to building supplemental disinfection.

The type of on-site disinfectant that is chosen plays a fundamental role in the control of Legionella throughout the building. The effect of the biocide is not limited to Legionella control but it could also have a significant impact on the plumbing system (corrosion issues) and the formation of unwanted disinfection by products (DBPs). For these reasons monochloramine has proven to be the best biocide that can be applied as secondary disinfectant. 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 disinfectants. Moreover it produces less disinfection by products, is minimally corrosive compared with chlorine and chlorine dioxide and it penetrates biofilm better leading to a complete an efficient disinfection (Treweek et al., 1985; Le Chevalier et al., 1993; McNeill et al., 2001).

3. Hot vs. Cold-water treatment

As explained in the previous paragraph, the type of disinfectant plays a crucial role on its effect against Legionella. This is not the only factor that drives the secondary disinfection treatment to be successful or not. The design of the biocide generator unit, how it is plumbed and in which system is connected are also factor that must be taken into account when speaking about supplemental disinfection.

One of the most asked question is, since Legionella does colonize only in warm water, if just the hot water of the building should be treated or the entire cold water coming into the facility (which includes both cold and hot water) has to be treated.

As a first thought, it could seem to make sense to add the biocide to all the water which is coming into the building because for sure it seems to be smarter to over-treat more water than the system that actually needs to be treated. However, chemistry and biology are not magic wands, and several scientific rules have to be respected. First of all, Legionella does not well colonize in cold water therefore treating all the cold water that comes into the building/facility is not efficient and could also present some severe issues.

Considering monochloramine, the injection of NH_2Cl to the cold water can lead to the modification of the microbiological environment and give rise to an increase of mycobacterium and coliforms populations upon impact of monochloramine, but this is still controversial, since recent publication show a different situation in building hot water systems (Duda et al., 2014). These complications have not been reported in the application of monochloramine on hot water if the residual is above 2 ppm (Duda et al., 2014; Casini et al., 2014). Dosing monochloramine on hot water only reduces the risk of nitrification since nitrifying bacteria are unlikely to colonize in hot water temperature environments.

Moreover, even though monochloramine is a very stable biocide, its injection in the cold water could lead to an accelerated decay. This is due to the fact that when part of the cold water is directed to the water heater it is subjected to a fast and sudden temperature increase, especially when steam water heater are used. The huge amount of heat which is transferred from the heat source to the water can increase the monochloramine decay rate. Although monochloramine presents almost no by-products, the decay path could form ammonia ion (NH_4^+) which remains dissolved into the water and can be an issue with copper pipes due to the formation of ammonia-copper complexes. If monochloramine is generated in hot water and directly injected upstream of hot water heat exchanger it is not subjected to this severe heat transfer, therefore the decay rate is greatly decreased and no by-product issue are present.

As already reported, monochloramine is effective for Legionella remediation with a residual concentration of 2- 3 mg/L. Monochloramine is synthesized from Hypochlorous acid (usually a stabilized hypochlorite solution) and ammonia or an ammonium salt (usually chloride or sulfate). Therefore, if all the cold water has to be treated and a residual concentration of 2- 3 mg/L has to be reached in the system, more monochloramine has to be produced. The cold and hot water installation diagrams are reported in Figure 3.
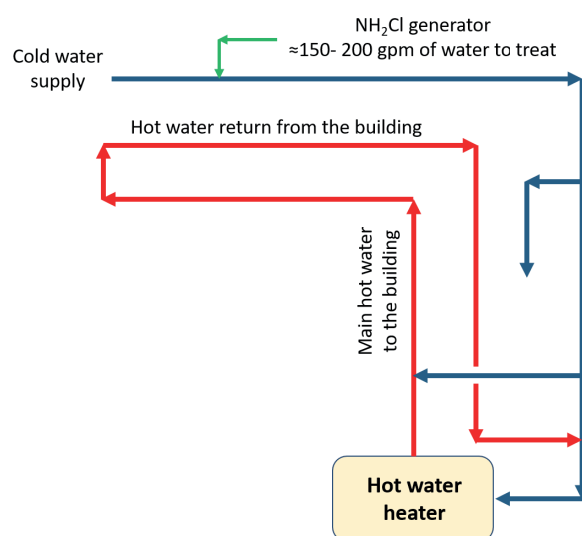
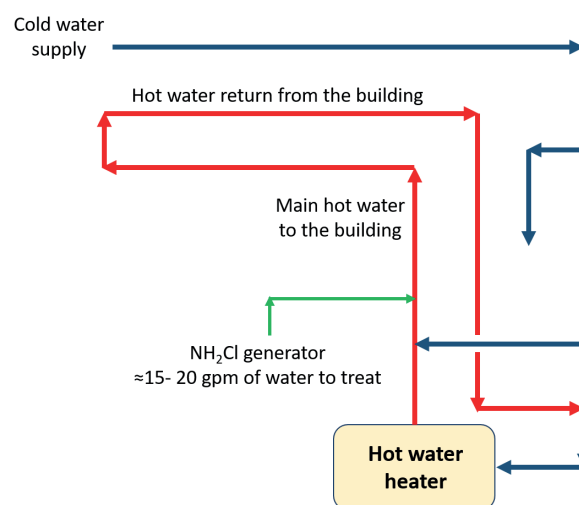**Cold water diagram:**   **Hot water diagram:**

Figure 3: Cold and hot water diagram installation.

It has been demonstrated that into a building the hot water usage is about 6- 10% of the total water. That means that to treat all the cold water, 10-12 times more monochloramine with respect to hot water has to be generated, and 10-12 times of the amount of chemicals have to be stored and used.

The increase in the amount of reagents leads to an increase in the operating costs. 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, monochloramine generator units able to produce up to 60 g/h of NH_2Cl are usually enough. On the other hand, if all the water as to be treated, units able to produce 800 g/h of monochloramine or more are needed.

Moreover, if a monochloramine generator is installed in the hot system, the water is always circulating thanks to the return pumps. That means that even though there is no hot water consumption i.e. during night hours, it is possible to trim the monochloramine production if needed and add NH_2Cl into the system via oxidation Reduction Potential (ORP) probes. 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 monochloramine is generated only when new water is flowing so no precursors can be added to maintain the monochloramine residual and stabilizer the free ammonia formation. If, for some reason, monochloramine must be added to the cold water entering the building the free ammonia formation in the cold water must be monitored closely and the monochloramine generator must be able to periodically feed free chlorine to combine with free ammonia if monitoring indicate the need. Additionally, there must be a system and method to stabilize the monochloramine in the hot water to prevent free ammonia formation in the hot water where the degradation rate of any oxidant is increased.

3

"NDMA formation: the real story"

1. A brief introduction on monochloramine disinfection

Monochloramine (NH_2Cl) is the most effective Cl-based disinfectant and is also the most materials respectful. It is effective at concentration of 2-3 mg/l where it 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.

Monochloramine is synthesized from hypochlorous acid and ammonia or an ammonium salt (usually chloride or sulfate) as follows in Eq. 1:

$$NH_3 + HClO \rightarrow NH_2Cl + H_2O$$
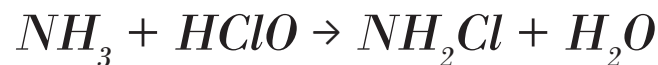
<div align="center">Equation 1</div>

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

Monochloramine has a low oxidant power with respect to other chlorine-based disinfectants due to the lower oxidation potential (ORP). This is not a drawback, however, because the stability and low reactivity of monochloramine helps it to better penetrate biofilms and kill bacteria that reside inside the biofilm. This is also 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 Chevalier et al., 1993; McNeill et al., 2001) thanks to several tests carried out by the Authors on different pipe materials like copper, galvanizer iron, stainless steel, PEx, PPr and C-PVC.

Due to higher oxidant power, chlorine attacks pipe materials (both metals and plastic) causing corrosion issues. Boffardi (Boffardi et al., 1992) showed that chlorine at concentrations above 0.5 ppm leads to iron corrosion in drinking water piping, while more recently two Authors (Hassinen et al., 2004; Castagnetti et al., 2010) demonstrated that chlorine is also corrosive on PE (polyethy-

lene) and PP (polypropylene) pipes which are becoming to be more and more common for water distribution piping.

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 byproducts. Higher concentration of THMs and HAAs were found when traditional chlorine-based disinfection technology 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, 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).

During the recent 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 $(R)_2$-N-N=O linked to the ammonia nitrogen atom. The most common nitrosamines are called NDMA, NDBA, NDEA, NDPA, NEMA, NMOR, NPIP and NPYR. These molecules are reported in Figure 1.
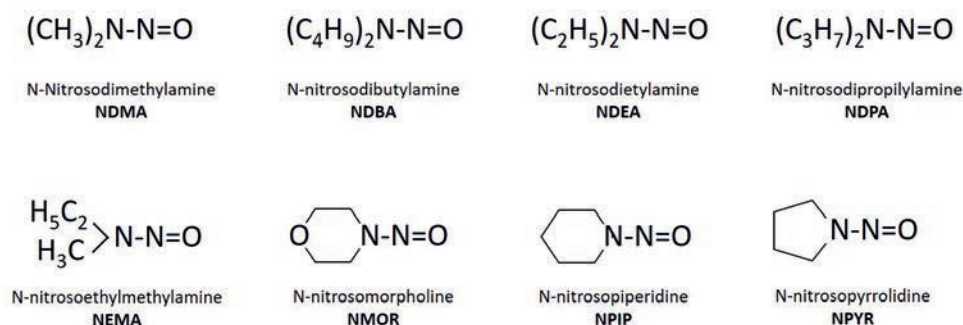

Figure 1: Most common nitrosamines.

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 2 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.
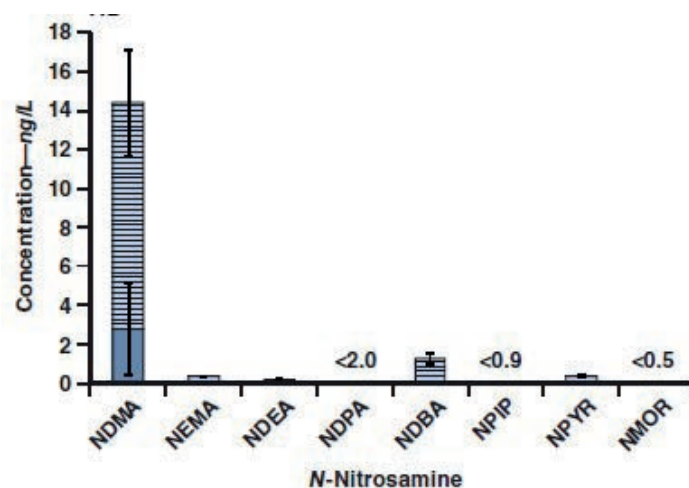
As a result, California's Department of Public Health did set a 10 ng/L notification level for three nistrosamines: NDEA, NDPA and NDMA (Russel et al., 2012).

During the recent years, 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 recorded 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.
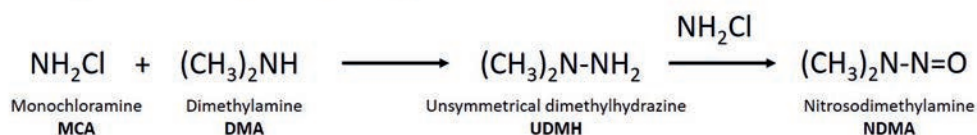
Monochloramine itself is not directly implied into the chemical process that leads to the formation of NDMA. As a weak oxidant, NH_2Cl performs its function as a biocide by killing bacteria and removing biofilm while preserving the piping construction materials. The formation of NDMA is not chemically involved in this biocidal action path. There are two main chemical reactions that leads to NDMA generation. In the first reaction path, proposed by Choi (Choi et al., 2002) monochloramine was reacting with dimethylamine to produce unsymmetrical dimethylhydrazine (UDMH). This specie was then further oxidized by monochloramine to NDMA.

The reaction path proposed by Choi was then further revised by Schreiber and Mitch (Schreiber et al., 2006). They researched the matter deeply in order to identify the correct chemical reactions and precursors. In particular, they demonstrate 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.

The old NDMA formation scheme proposed by Choi and the revised one confirmed by Schreiber and Mitch are reported hereinafter in Figure 3.
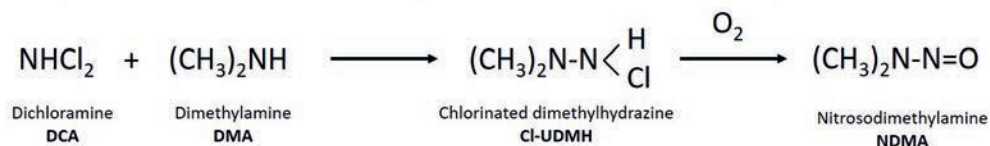

Figure 3: Old (1) ad new (2) approaches for the NDMA formation.

This second path reported in Figure 3 confirms that monochloramine is not involved into the NDMA formation process. Despite the fact, some researchers link the presence of NDMA with the use of chloramination process for water disinfection.

3. The chemistry of monochloramine

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

As reported in Eq. 1, 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_{NH_2Cl} = $1.5 \cdot 10^{10}$ $M^{-1}h^{-1}$ (Morris et al., 1981). This very high number suggests that once monochloramine precursors come in contact, NH_2Cl is generated faster than other by-products such as dichloramine and free ammonia, since the other reaction's kinetic constant are, at least, three orders of magnitude smaller.

Factors that influence the 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 chloraminaion process. This because the pH value of the water plays a key role in the equilibria between hypochlorous acid (HClO) and its dissociate form, the hypochlorite ion (OCl^-).

The equilibria between the two species, referred as % of HClO available, is presented in Figure 4.
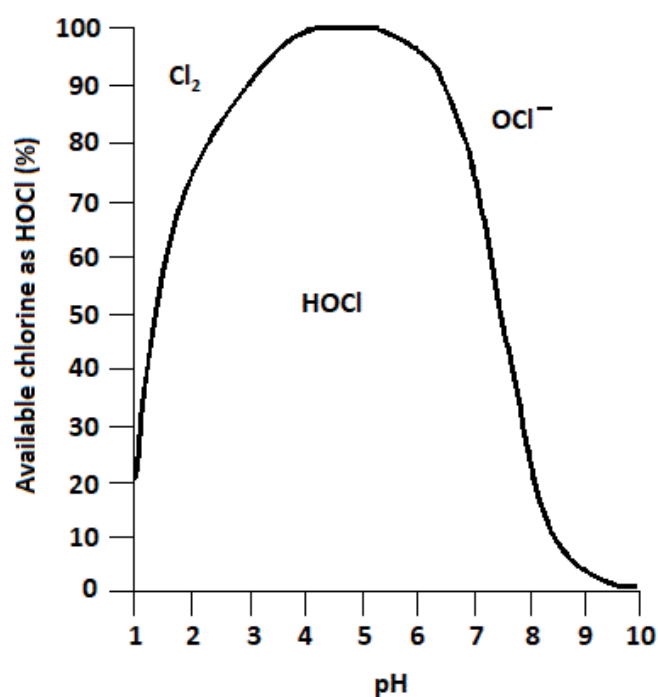

Figure 4: Chlorine, hypochlorous acid and hypochlorite ion equilibria at different pH values.

As reported in the previous paragraph 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-tri-chlorinated compounds.

In fact, at pH level lower than 7.2, in addition to NH_2Cl formation, the greater % of HOCl could favor the dichloramine formation, by reaction Eq. 2:
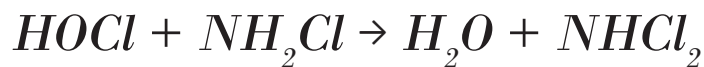
$$HOCl + NH_2Cl \rightarrow H_2O + NHCl_2$$
<center>Equation 2</center>

Dichloramine is then susceptible to degradation by monochloramine. This oxidation reaction leads to the formation of gaseous nitrogen, through the following reaction Eq. 3:
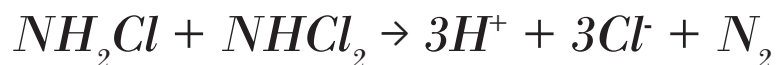
$$NH_2Cl + NHCl_2 \rightarrow 3H^+ + 3Cl^- + N_2$$
<center>Equation 3</center>

Moreover, this reaction produces an acid specie (dissociated HCl) which additionally lower the pH value, by 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 proved to be one of the two NDMA precursors.

In addition to the favored monochloramine formation at pH values typical for drinking water, this biocide can take advantage of a great and 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 concentrations and CO_3^{2-} concentration).

In Figure 5-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 levels are around 2-3 ppm (0.05 mM), monochloramine levels remained stable for the whole duration of the test ($\approx$ 170 h). Only concentrations higher than the drinking water range (> 5 ppm) resulted in a small loss of NH_2Cl during the test.

In Figure 5-B, Vikesland evaluated 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 $\approx$ 170
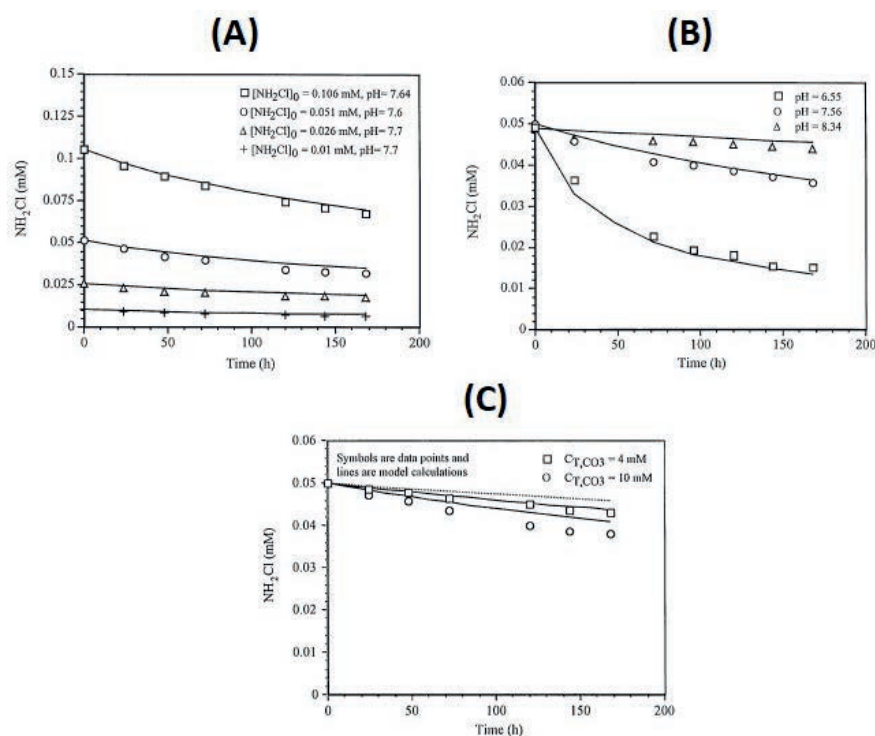
Figure 5: Monochloramine stability over time at, (A): different NH$_2$Cl concentrations, (B): different pH, (C): different CO$_3^{2-}$ concentrations (Vikesland P. J. et al., Water Resources, 2001, 35, 1766-1776).

h was measured due to hydrolysis reaction, while at pH= 8.34, monochloramine was completely stable over the whole duration of the test.

Figure 5-C shows the influence of the total carbonate concentration of monochloramine stability. These tests were carried out since the presence of acid catalysts like phosphate, sulfate, and acetic acid can accelerate monochloramine decay by catalyzing monochloramine disproportionation. Carbonate ions (CO$_3^{2-}$) could act like an acid catalyst dependently on the pH level, since at low pH values the dissociation equilibria of carbonic acid is left shifted, and acid species are present (carbonic acid and mostly bicarbonate at pH between 7- 8).
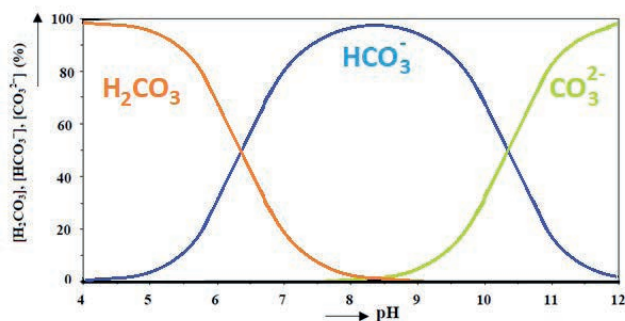

Figure 6: Distribution of the carbonic fraction as percentages of the total carbon content at different pH (Greenwood et al., Chemistry of the Elements (2nd ed.). Butterworth-Heinemann, 1997, ISBN 0-08-037941-9).

In drinking water range, as shown in Figure 5-C (pH≈ 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.

The results reported in Figure 5-A-B-C confirm that monochloramine is a stable molecule in drinking water parameters ranges. This is another confirmation that it is not 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 if Figure 7.
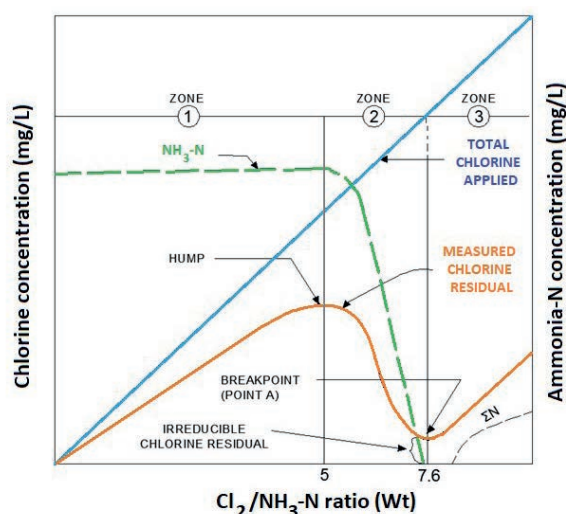

Figure 7: Breakpoint curve (Saunier B. M. et al., Journal AWWA, 1979, 71, 164-172).

Initially, chlorine residual (orange line) increases in the monochloramine region up to a Cl_2/NH_3-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).

This is further proof that if during a chloramination process all the parameters are respected, only monochloramine will be generated, without the incursion of side reactions, by-products formation and stability.

4. Why there is 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 includes rivers, lake and smaller water streams, while the second is 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 depress the bacterial content in the 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 in order 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 in order to avoid a 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 plants 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 8.
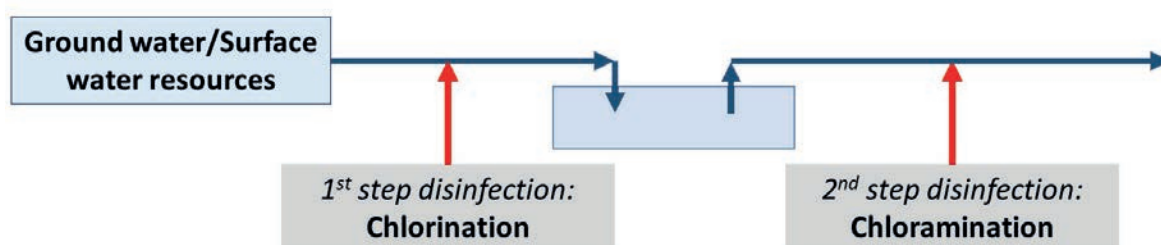
Figure 8: Scheme of an industrial chloramination process.

Woods (Woods et al., 2015) carried out a study in which she was monitoring and measuring the NDMA levels 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.

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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 implied in the formation of NDMA.

The first consideration that has to be taken in the paper proposed by Woods, is that she related the occurrence of nitrosodimethylamine as a function of the type of water source that is fed to the plant. In particular, she measured NDMA levels and compared the results of water disinfection plants that are treating either surface water or ground water. The Author reported that groundwater, as a source water, had a frequency of occurrence of 3.3 % 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 where she measured the NDMA levels in surface and groundwater treated with chloramine in wester Australia. The result showed that NDMA was much more likely to be found in surface water resources.

The reason 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 intended to be classical organic molecules, but also organisms that over a long period of time can decompose into organic compounds that can lead to the NDMA formation. The greater presence of animals, organisms, and dissolved oxygen into surface water resources the more suitable the environment for the formation of NDMA precursors.

Moreover, looking at the chemistry of monochloramine, how 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 characteristic and andvantages 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 et al., 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 maintain the same standards as smaller applications. For this reason it is possible that in some areas of the water treated the proper stoichiometric ratio between the two reagents is not respected, in this case dichloramine can

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be created.

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 e al., 2017) evaluated the reduction of the NDMA formation potential by carrying out different experimental tests where he evaluated 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 polymers in order to replace alum and synthetic polyDADMAC since this last chemical proved to contribute to NDMA precursors. Also, Prescott (Prescott et al., 2017) highlighted how wastewater treatment plants are the major source of precursors for the formation of NDMA.

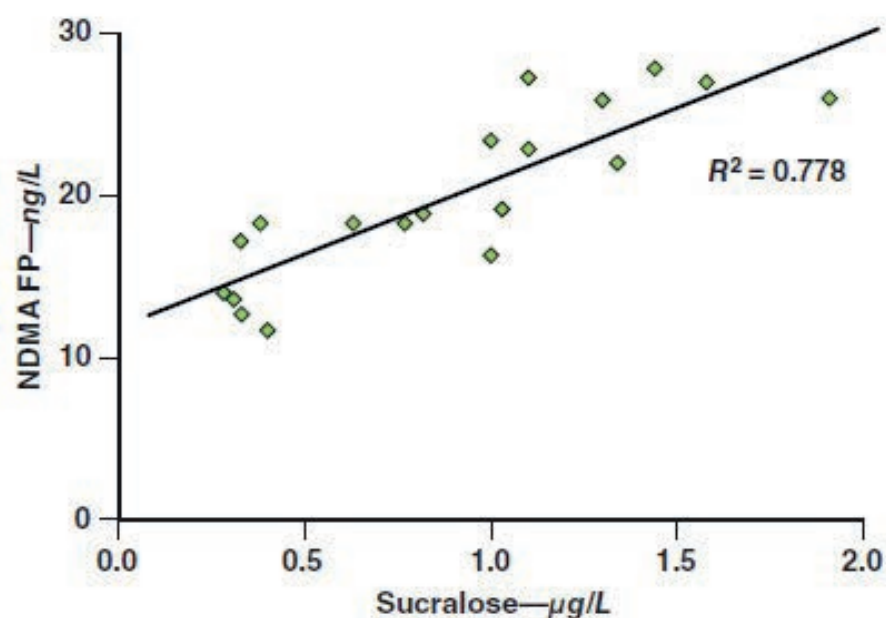Figure 9: Relationship between sucralose concentration in wastewater treatment plants and NDMA formation potential (Prescott M. et al., Journal AWWA, 2017, 109, 243-251).

In particular, Prescott demonstrated how the NDMA presence is directly related to the amount of sucralose present in the wastewater treated. The greater the amount of sucralose detected, the higher the NDMA formation potential.

5. Conclusion

The purpose of this paper 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 in respect to traditional chlorine based disinfection techniques and NH2Cl 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 like 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 present in surface waters due to the presence of animals like birds and fish. The second reason is that in an improper generation of monochloramine, where the reagents are not properly balanced the formation of dichloramine that can further react and convert other precursors into NDMA.

Therefore, the true focus to decrease the NDMA levels and avoid 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.

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