

# Effects of pipe materials, orthophosphate, and flow conditions on chloramine decay and NDMA formation in modified pipe loops

Hong Zhang and Susan A. Andrews

## ABSTRACT

This study examined the effects of pipe materials (iron, copper, lead and PVC) and orthophosphate on chloramine decay and *N*-nitrosodimethylamine (NDMA) formation under stagnant, laminar and turbulent conditions using modified pipe loops. As expected, chloramine decay rates generally increased with increasing flow velocity. In the presence of orthophosphate, chloramine degradation in the iron loop increased regardless of flow conditions, whereas chloramine decay rates decreased for the copper and lead loops, especially under turbulent conditions. NDMA formation in the copper loop was consistently higher than it was in the PVC control loop under laminar conditions, supporting the theory of a possible catalytic effect of copper on NDMA formation (as reported elsewhere). Iron catalysis of NDMA formation became more prominent in the presence of orthophosphate, but copper catalysis became less significant after the addition of orthophosphate. Only in the copper loop, the released metal concentrations were decreased under laminar conditions compared with turbulent flow, and they were also reduced effectively due to the addition of orthophosphate, suggesting that the catalytic effect was not primarily due to dissolved copper but likely included copper-based solids (corrosion products).

**Key words** | chloramine, copper, iron, lead, modified pipe loop, *N*-nitrosodimethylamine

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## INTRODUCTION

The application of a secondary disinfectant in distribution systems is to maintain the microbial stability of the treated water. However, secondary disinfectants may experience temporal and spatial degradation in distribution systems due to chemical and biological reactions that occur in the bulk water and on the pipe wall. Therefore, the overall disinfectant decay within a pipe is usually postulated as a pseudo-first-order reaction consisting of parallel reactions occurring in the bulk flow and on the pipe wall (Rossman *et al.* 1994). Generally, both bulk water and pipe wall disinfectant decay rates increase with increasing flow velocity as a result of an increased mass transfer rate of disinfectant residual to the pipe surface, and/or an increased release rate of corrosion products from the pipe surface (Hallam *et al.* 2002; Digiano & Zhang 2005; Mutoti *et al.* 2007; Westbrook & Digiano 2009).

Recently, combined chlorine has received growing attention by water utilities that are challenged to comply with the Stage 2 Disinfectant/Disinfection Byproducts Rule D/DBPR. The advantages of applying combined chlorine as an alternative to free chlorine include a minimized production of trihalomethanes (THMs) and haloacetic acids (HAAs), and a relatively stable residual in distribution systems. However, combined chlorine (mainly monochloramine) can potentially increase the formation of nitrosamines (Najm & Trussell 2001; Choi *et al.* 2002), of which *N*-nitrosodimethylamine (NDMA) is the major species of interest. The occurrence of nitrification and elevated lead release have also been observed in chloraminated distribution systems (Wilczak *et al.* 1996; Vasquez *et al.* 2006).

Considerable effort has been made to investigate factors affecting disinfection byproduct (DBP) formation in

distribution systems. These factors include the concentration and chemical properties of the DBP precursors, water temperature, pH, disinfectant type, dose and residual and contact time (Rossman *et al.* 2001; Liang & Singer 2003; Baribeau *et al.* 2005). Metal pipe materials and their corrosion byproducts may also affect the formation and the fate of halogenated DBPs in distribution systems as has been reported for iron and copper-based pipes by Li *et al.* (2007), Zhang & Andrews (2012) and Rossman *et al.* (2001). However, no relevant information concerning the impacts of pipe deposits on nitrosamine formation has been reported at the time of writing, and the literature concerning the fate of nitrosamines in full-scale distribution systems is varied (Wilczak *et al.* 2003; Baribeau *et al.* 2006; Charrois *et al.* 2007). In addition, given the impacts of flow conditions on chloramine degradation and that chloramine concentration is a rate-limiting factor for NDMA formation, the impacts of flow conditions on NDMA formation merits some investigation.

Therefore, the objective of this study was to evaluate the impacts of pipe materials (ductile iron, PVC, copper and lead) on chloramine stability and NDMA formation in the absence and presence of orthophosphate as a corrosion inhibitor and, in particular, under different flow conditions. These pipe materials are widely present in either water mains (such as ductile iron and PVC) or household plumbing systems (such as copper), and lead can be commonly found in old lead service lines, soldered joints and brass plumbing fittings. Modified pipe loops were used in the tests under typical chloramination conditions. The results of this study improve our understanding about key factors that affect chloramine stability and NDMA formation in the complex physiochemical and biological environment of distribution systems.

## MATERIALS AND METHODS

### Reagents and materials

All chemicals used in this study were American Chemical Society grade or higher. Orthophosphate ( $K_3PO_4$ ) was the corrosion inhibitor selected for testing. The test water was the chloraminated reservoir effluent from the Mannheim

Water Treatment Plant (MWTP), Ontario. The chloramine concentration in the test water ranged from 1.3 to 1.6 mg/L as  $Cl_2$ , and other water quality parameters in the test water are listed in Table 1.

Due to the consistently low formation of NDMA in the test water, one NDMA precursor, dimethylamine (DMA; purchased from Sigma-Aldrich), was spiked to ensure NDMA formation at a measurable level ( $>1$  ng/L). A dosing solution containing DMA and/or orthophosphate was prepared by adding 1 mL of 25 g/L (0.56 M) DMA and/or 20 g  $K_3PO_4$  into 25 L unchloraminated post-filtration water from the MWTP. The target concentrations of orthophosphate and DMA in the influent were 1 mg/L as P and 20  $\mu$ g/L (450 nM), respectively.

### Modified pipe loops

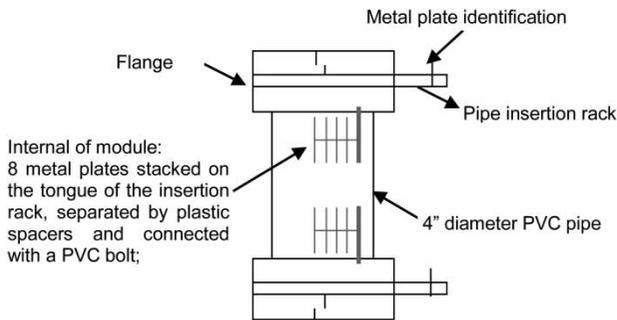
Dalhousie pipe loops that were designed and manufactured by Dr Gagnon's research group (Gagnon *et al.* 2008) were modified according to Cantor (2009) to increase their efficiency and expand the range of operating conditions. Sixteen square test coupons ( $6.4 \times 6.4 \times 0.16$  cm; Metal Samples Co., Alabama, USA) were stacked inside 10 cm (ID) Schedule 40 PVC pipes to create test modules. The module construction is shown in Figure 1. The main module design parameters are summarized in Table 2. The lengths of the PVC-, iron-, copper- and lead-containing modules were determined based on volume-to-surface area ratios commonly observed in water mains and residential plumbing systems.

The modified pipe loops are illustrated in Figure 2. Each pipe loop consisted of six components: the test module, the recirculating pump, the return section, the aluminium

**Table 1** | Summary of water quality parameters for the influent of the pipe loops

Parameters	Values
pH	$7.4 \pm 0.1$
Alkalinity (mg/L)	$224 \pm 11$
UV <sub>254</sub> ( $cm^{-1}$ )	$0.039 \pm 0.007$
TOC (mg/L)	$2.58 \pm 0.25$
SUVA ( $L/mg\ cm^{-1}$ )	$0.015 \pm 0.003$
Ammonia (mg/L as N)	$0.17 \pm 0.05$
Nitrate (mg/L as N)	$4.06 \pm 0.34$

TOC: total organic carbon; SUVA: specific ultraviolet absorption.



**Figure 1** | Module configuration (adapted from Cantor (2009)).

**Table 2** | Summary of design parameters for pipe loops

	V/S <sup>a</sup> (mL/cm <sup>2</sup> )	Module length (cm)	No. of plates	Equivalent distribution system pipe diameter (cm)
PVC	3.0	52	0	12
Iron	3.1	53	16	12
Copper	1.5	26	16	6
Lead	1.6	28	16	6

<sup>a</sup>Volume-to-surface area ratio.

support frame, the influent feed pump and the influent and effluent ports. A PVC flexible hose was used as the return section. The influent port was located on the return section and was the connection point for the influent feed pump to provide fresh water to the pipe loop. The effluent port was located on the module and acted as both a sample collection point and the outflow of the water. The test water was introduced into the pipe loop by the influent feed pump, the flow rate of which was adjusted based on the desired retention time and the volume of the pipe loop. The recirculating pump propelled the water through the

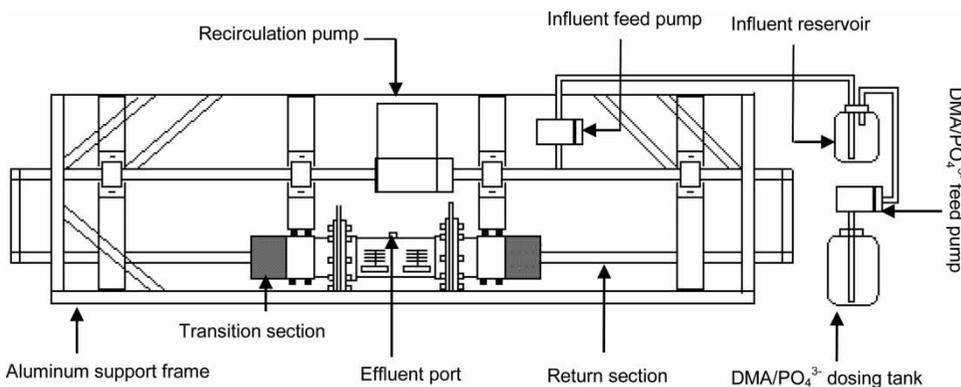
pipe loop to provide the desired velocity (typically 0.3 m/s) within the test section.

## Experimental procedures

After the pipe loops were modified, they were first flushed with the chloraminated reservoir effluent for 3 days, and then conditioned for periods of up to 120 days to allow released metal concentrations to stabilize in the test water matrix. During conditioning, the flow rates in the four pipe loops were increased stepwise to obtain hydraulic retention times (HRTs) of 12, 6 and 2 hours. To eliminate chlorine demand from the newly installed pipes, a high concentration of free chlorine (390 mg/L) was pumped into the loops at a flow rate of 30–38 mL/min for 3 hours. Due to a persistently high chlorine demand in the copper loop, another two conditioning treatments (180 mg/L free chlorine, 10 days) were conducted for that loop.

Experiments were performed in two phases: first, without the addition of orthophosphate and then with the addition of 1 mg/L orthophosphate. In each phase, three flow regimes typically encountered in distribution systems were examined – turbulent, laminar and stagnant. Turbulent and laminar flow conditions were achieved by turning on and off the recirculating pumps, resulting in flows with Reynolds numbers (Re) of approximately 30,000 and <10, respectively. HRTs in each pipe loop were varied by adjusting the influent feed pump flow rate. The stagnant flow condition was achieved by turning off both the influent feed pump and the recirculating pump.

Water samples from the influent and the effluents of the four pipe loops were collected three times a week



**Figure 2** | Schematic of the modified pipe loop (not to scale).

for chloramine, released metal concentrations and NDMA measurement. pH, phosphate, ammonia, nitrite and nitrate in the influent and the effluents of the four pipe loops were also measured but at a frequency of once a week. Throughout the entire experiment, the pH values of the effluents from the four pipe loops ranged from pH 7.2 to pH 7.6, exhibiting no significant changes relative to the influent pH. Variations in the values of the other parameters will be discussed along with the results for chloramine, metal and NDMA concentrations. In addition, to ensure a relatively constant concentration of DMA being dosed into the test water, the flow rates of the DMA dosing solution and the reservoir effluent were monitored on each sampling date. The DMA concentration being dosed into the influent water was also checked before and after the addition of orthophosphate by monitoring the 24 hour NDMA formation in 1 L amber bottles with the ambient chloramine concentration.

Measurement of total organic carbon (TOC) concentration was undertaken using a Model 1030 TOC analyser (OI Analytical, USA).  $UV_{254}$  was measured using a CE 3055 Reflectance Spectrophotometer (Cecil Instruments, UK) at 254 nm. Measurements of total chlorine and ammonia were performed using a Hach DR2700 spectrophotometer (Hach Company, USA) at 530 and 425 nm, respectively. Routinely, total chlorine was measured instead of monochloramine because of greater temperature dependency of the monochloramine test; however, the total chlorine residuals were shown to consist almost exclusively of monochloramine. Metal concentrations were analysed using a Varian SpectrAA.20 Flame Atomic Absorption Spectrometer (Agilent Technologies, USA) after being acidified to pH <2. Nitrite, nitrate and phosphate concentrations were measured using a Dionex DX-300 Series Ion Chromatography System (Thermo Scientific, USA). NDMA extract preparation was carried out according to Taguchi *et al.* (1994), and the instrument used for NDMA analysis was a Varian 4000 gas chromatograph/mass spectrometer (Agilent Technologies, USA).

## RESULTS AND DISCUSSION

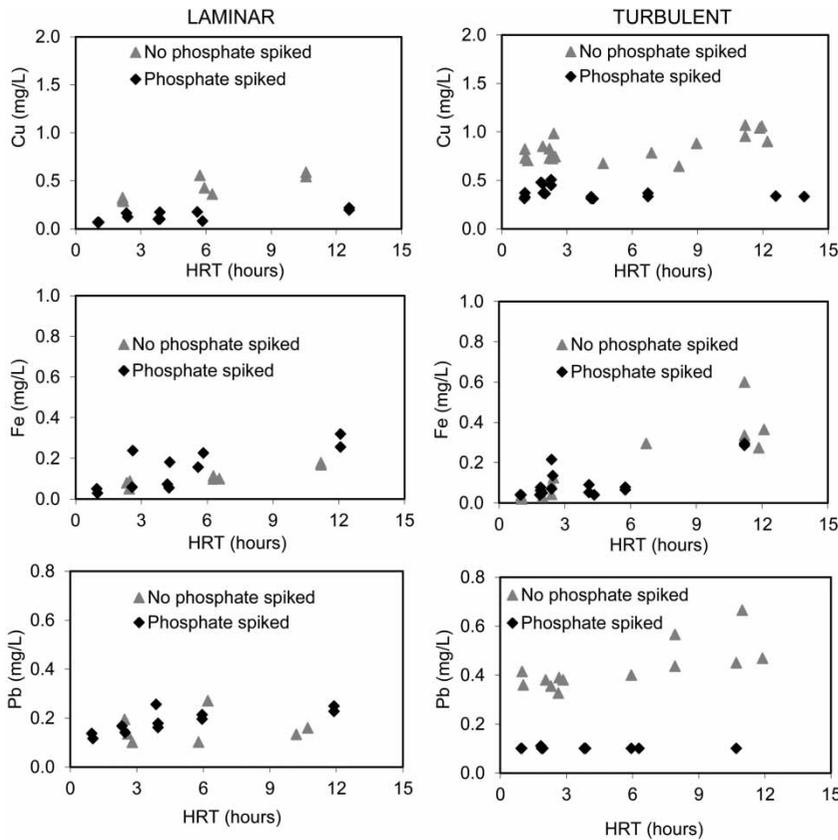
The effects of pipe materials (iron, copper, lead and PVC), orthophosphate and flow conditions on chloramine stability

and NDMA formation were examined using a set of modified pipe loops installed at a water treatment plant. By taking samples concurrently from each loop, it was possible to make direct comparisons of released metal concentrations, chloramine degradation and NDMA formation in the absence and presence of orthophosphate under different flow conditions. The results will be discussed starting with metal and inorganic nitrogen species concentrations, primarily because most of the observations were consistent with those of other researchers and can be well explained by previously proposed theory and/or mechanisms in the literature. This provides a measure of confidence in the testing procedures since some metal and nitrogen species have been shown to affect chloramine decay and byproduct formation. It also provides a summary of data that will be referred back to in subsequent sections when interpreting the trends concerning chloramine stability and NDMA formation.

### Metal and inorganic nitrogen species concentrations

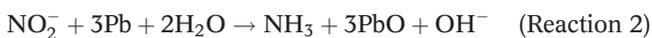
Figure 3 compares metal concentrations in the absence and presence of orthophosphate under laminar and turbulent flow conditions, and shows that the results varied with both the type of pipe material employed and the hydraulic conditions present. Released copper concentrations significantly decreased after the addition of orthophosphate under both laminar and turbulent conditions, as expected (Edwards *et al.* 2002). Also, as expected, orthophosphate did not exhibit obviously beneficial effects on iron corrosion control under either laminar or turbulent conditions, as also evidenced by McNeill & Edwards (2000, 2001). However, released lead concentrations were effectively reduced by the presence of orthophosphate, but mainly when the water was turbulent. In the absence of orthophosphate, the released lead concentrations varied from 0.4 to 0.6 mg/L in turbulent water, but they were below 0.1 mg/L after the addition of orthophosphate. Under laminar conditions, there were no significant differences in lead concentrations before and after the addition of orthophosphate (varying between 0.1 and 0.2 mg/L).

Given that orthophosphate previously has been shown to effectively decrease lead release (Edwards *et al.* 1999; Edwards & McNeill 2002), the observed relative



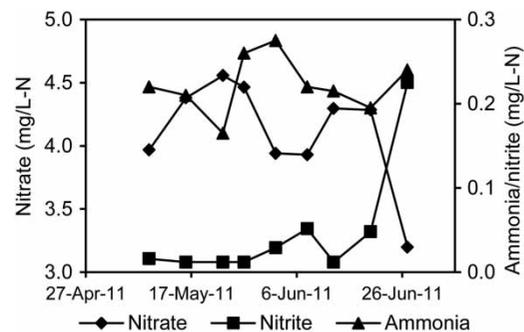
**Figure 3** | Metal concentrations in the pipes of copper, iron and lead in the absence and presence of 1 mg/L orthophosphate under two flow conditions.

ineffectiveness of orthophosphate on lead corrosion control under laminar conditions in the current study was unusual. However, it might be explained by the relative newness of the module materials (leading to higher than normal lead release rates) and/or interplays among lead and dissolved species such as ammonia, nitrite and nitrate (Uchida & Okuwaki 1998; Edwards & Dudi 2004; Zhang *et al.* 2009a) as shown in Reactions 1 and 2:



According to these reactions, free ammonia from the application of monochloramine combined with a high concentration of nitrate may have synergistically increased the lead corrosion by interfering with the formation of the passive PbO layer on its surface. If this phenomenon was occurring, then according to Reactions 1 and 2, there

should be a strong correlation among the concentrations of the three nitrogen species. Namely, a decrease in nitrate concentrations should lead to an increase in both nitrite and ammonia concentrations. Figure 4 illustrates the variations in the nitrogen species concentrations measured in the lead loop, confirming that decreases in nitrate concentrations were associated with increases in both nitrite and ammonia concentrations and providing evidence for the



**Figure 4** | Variations of nitrate, nitrite and ammonia in the lead loop.

potential occurrence of Reactions 1 and 2 in the lead loop. The co-presence of ammonia, nitrite and nitrate in significant concentrations in the lead loop may also suggest the occurrence of nitrification as a potential source of these ions, but microbiological confirmation of this was beyond the scope of the study and requires further investigation.

The results of Figure 3 also indicate some seemingly confounding effects from orthophosphate and the type of pipe materials employed, but these effects appear to be mainly related to the flow conditions present. For example, released copper concentrations were lower under laminar conditions compared with those under turbulent conditions, regardless of orthophosphate addition. Lower released iron and lead concentrations were also observed under laminar conditions but only in the absence of orthophosphate. These observations are consistent with previous studies in that high flow rates can loosen the corrosion byproducts deposited on the pipe wall and cause more metal to be released from the pipe surface (Mutoti *et al.* 2007). Interestingly, the released lead concentrations decreased by up to 50% under turbulent conditions compared with laminar flow after orthophosphate was added, which was different from the observations from other studies (Xie & Giammar 2011). It will be shown later that more nitrite ions were present under laminar flow than under turbulent conditions (e.g., see section on Chloramine decay). As such, the observed lower lead concentrations in phosphate-containing

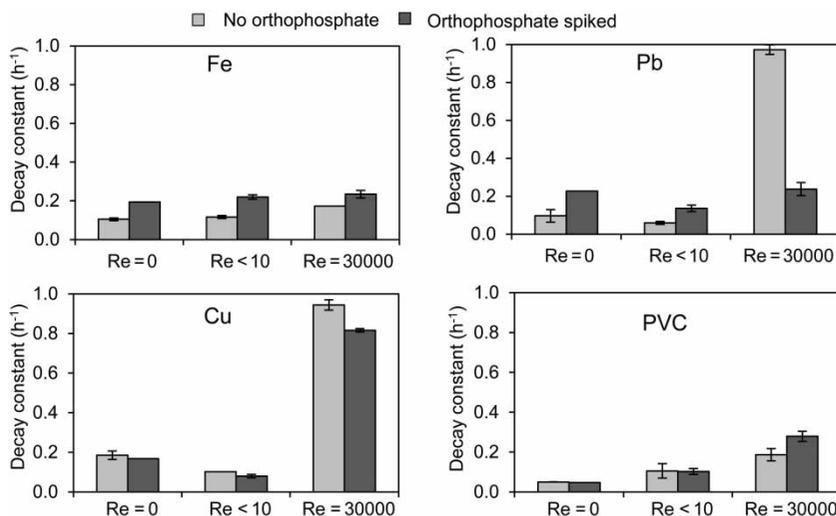
water under turbulent conditions than under laminar conditions was most likely due to the interplays between nitrite presence and lead corrosion as discussed earlier (Reactions 1 and 2).

### Chloramine decay

Generally, chloramine concentrations in the four pipe loops all followed pseudo-first-order decay kinetics. Decay constants were estimated by fitting a pseudo-first-order decay equation to the chloramine data using Microsoft Excel and used to evaluate changes in chloramine stability resulting from the different conditions tested.

### Effects of flow conditions, pipe materials and orthophosphate presence

Figure 5 displays pseudo-first-order chloramine decay constants for the four pipe materials before and after the addition of orthophosphate under three flow regimes (Reynolds numbers of  $Re = 30,000$ ,  $Re < 10$  and  $Re = 0$ ). In addition, for each pipe material, a Fisher's least significant difference (LSD) test at a confidence level of 95% was applied to pairs of chloramine decay constants that were obtained with different treatments to estimate the significance of the effects of different flow conditions and the presence or absence of orthophosphate on chloramine



**Figure 5** | Pseudo-first-order chloramine decay constants for the four pipe loops under different flow conditions, initial chloramine 1.3 ~ 1.6 mg/L as  $Cl_2$ , error bars indicate the measured maximum and minimum values ( $n = 2$ ).

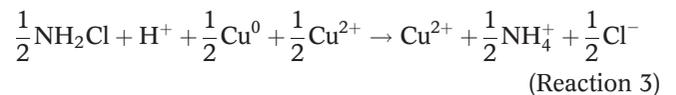
decay (Montgomery 2000). The results of the LSD tests are summarized in Table 3.

Generally, chloramine decay constants for all four pipe materials increased with increasing water flow. This agrees with previous findings that an increase in flow velocity increases the mass transfer rate of chloramine to the pipe surface and/or increases the release rate of metal corrosion products from the pipe surface, thereby increasing chloramine consumption (Rossman *et al.* 1994; Westbrook & Digiano 2009). The results for the PVC loop also agree with a previous finding that bulk chlorine decay rates are dependent on flow velocity (Menaia *et al.* 2003).

The extent to which the decay constants were affected by flow rate was also influenced by the type of pipe material present. As shown in Figure 5, there was a marked increase in chloramine decay in both the lead and copper pipes under turbulent conditions. A rapid loss of chloramine was observed to occur in the initial 1–2 hours of the tests during which time approximately 70% of chloramine was degraded. In the lead loop, the chloramine decay may have also been enhanced by the presence of nitrate in the water. As discussed in the previous section, the capability of lead to react with nitrate and form nitrite has been well documented (Reaction 1; Uchida & Okuwaki 1998; Edwards & Dudi 2004; Zhang *et al.* 2009). Under turbulent

conditions, up to 0.08 mg/L nitrite as N and 0.4 mg/L Pb (Figure 3) were detected in the lead pipe in the absence of orthophosphate, and they were 40 and 75% higher, respectively, than those in the presence of orthophosphate. Since chloramine reacts with  $\text{NO}_2^-$  and considering that  $\text{NO}_2^-$  is formed in Reaction 1, it was reasonable to have observed accelerated chloramine degradation in the lead loop.

The high chloramine demand in the copper pipe under turbulent conditions is consistent with previous findings that chloramine can be rapidly consumed by copper corrosion via the following reaction (Nguyen 2005):



Under turbulent conditions, the copper surface can be scoured, exposing fresh copper and providing a virtually unlimited supply of metallic copper ( $\text{Cu}^0$ ) to participate in this reaction. The observed rapid chloramine decay under these conditions was, therefore, not unexpected.

To evaluate the significance of the presence or absence of orthophosphate on chloramine decay, the LSD tests were also applied to those pairs of decay constants and the results are summarized in Table 4. As shown in

**Table 3** | Significance of the effects of flow conditions on chloramine decay determined by the LSD test (95% confidence level)

Treatments compared				Fe	Pb	Cu	PVC
No orthophosphate	Re = 0	→	Re < 10	×	×	↓	×
	Re < 10	→	Re = 30,000	↑	↓	↑	↑
	Re = 0	→	Re = 30,000	↑	↑	↑	↑
Orthophosphate spiked	Re = 0	→	Re < 10	↑	↓	↓	↑
	Re < 10	→	Re = 30,000	↑	×	↑	↑
	Re = 0	→	Re = 30,000	×	↑	↑	↑

Note: ×, no significant effect; ↑, increasing decay; ↓, decreasing decay.

**Table 4** | Significance of the effects of orthophosphate on chloramine decay determined by the LSD test (a confidence level of 95%)

Materials	Treatments	Re = 0	Re < 10	Re = 30,000
Fe		↑	↑	↑
Pb	No orthophosphate → Orthophosphate spiked	↑	↑	↓
Cu		×	×	↓
PVC		×	×	↑

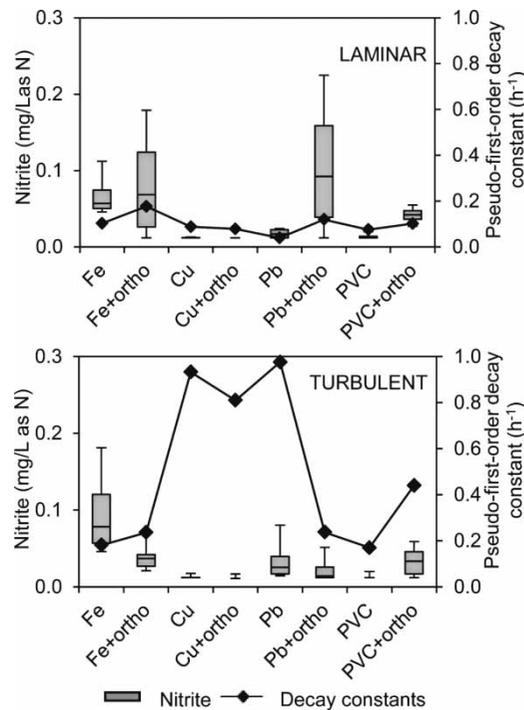
Note: ×, no significant effect; ↑, increasing decay; ↓, decreasing decay.

Table 4 and also in Figure 5, chloramine degradation did not exhibit statistically significant changes upon the addition of orthophosphate for stagnant or laminar flow conditions ( $Re = 0$  and  $Re < 10$ , respectively) for both the copper and PVC loops. However, under turbulent flow ( $Re = 30,000$ ), chloramine degradation in the copper loop decreased in the presence of orthophosphate, and the opposite effect was observed in the PVC loop. Surprisingly, in orthophosphate-treated water, chloramine decay significantly increased in the iron and lead loops, but only under no flow or low flow conditions ( $Re = 0$  and  $Re < 10$ ) for the lead loop.

Comparing the results in Figures 3 and 5 reveals that while chloramine decay was significantly increased in the presence of orthophosphate (in the iron and lead loops), metal release kinetics remained comparable before and after the addition of orthophosphate. This suggests that, rather than metal corrosion processes, other factors (e.g., nitrite formation) may have played an important role in accelerating chloramine decay. Further discussion of this theory is provided in the following section.

### Chloramine decay and nitrite formation

The relationships between nitrite ( $\text{NO}_2^-$ ) concentrations and chloramine decay for each type of pipe material present were further investigated in this study and are illustrated in Figure 6. Nitrite ( $\text{NO}_2^-$ ) may be present from either or both of abiotic reactions (e.g., Reaction 1 when in contact with lead) and from nitrification (Wilczak *et al.* 1996), and although the presence of nitrifiers could not be detected directly in this study, nitrite concentrations were measured in the influent and effluents of the four pipe loops. Due to consistently low occurrence of nitrite in the influent ( $< 0.012$  mg/L as N), only the effluent nitrite concentrations are plotted in Figure 6 along with their corresponding chloramine pseudo-first-order decay constants for two tested flow conditions (turbulent and laminar). The considerable formation of nitrite in the iron, lead and PVC loops regardless of orthophosphate presence or flow conditions suggests the presence of at least some nitrification during this study. In general, high nitrite concentrations corresponded to rapid chloramine degradation constants under both laminar and turbulent conditions, as expected.



**Figure 6** | Box and whisker plots for nitrite concentrations before and after the addition of orthophosphate overlaid with pseudo-first-order chloramine decay rate constants, laminar flow ( $n = 5$ ), turbulent flow ( $n = 6$ ). The top and bottom of the box represent the 75th and 25th percentile, respectively, while the whiskers represent the maximum and minimum values.

In addition, under laminar conditions, the iron and lead loops exposed to orthophosphate had a relatively higher concentration of nitrite ( $\sim 0.2$  mg/L) compared with other pipe materials (mostly below 0.05 mg/L). This was in agreement with previous findings that orthophosphate can enhance nitrification and, therefore, nitrite formation (Zhang & Edwards 2010). However, the measured nitrite concentration did not always increase with the addition of orthophosphate, as observed for the iron and lead loops under turbulent flow conditions. Turbulent flow can disturb the stability of biofilms where nitrifiers could be present, thereby decreasing their activity (Zhang *et al.* 2009b). Decreased nitrite formation in the lead loop after the addition of orthophosphate under turbulent conditions is also likely because the protective layer on the lead surface decreased the exposure of lead to nitrate in the water (Reaction 1).

Nitrite concentrations in the copper loop were consistently lower than in the other loops, with the maximum concentrations for both flow conditions being below

0.02 mg/L (Figure 6). It is known that high levels of copper (>0.1 mg/L) are toxic to nitrifiers, thereby inhibiting nitrification (Zhang *et al.* 2009b) and the measured copper concentrations in this study ranged from 0.08 to 1.0 mg/L (Figure 3). The lack of nitrite in the copper loop also suggests that abiotic consumption of chloramine due to copper corrosion (Reaction 3) was a likely reason for the rapid chloramine dissipation under turbulent flow (Figure 5).

### NDMA formation

In addition to determining the potential effects of pipe materials, orthophosphate and flow conditions on NDMA formation, the pipe loops were operated at different HRTs to evaluate the impacts of reaction time and provide additional confirmation of the observed results.

### Effects of flow conditions

Figure 7 provides a general overview of the results by comparing NDMA concentrations in the effluent of the four pipe loops in the absence of orthophosphate under turbulent ( $Re = 30,000$ ) and laminar ( $Re < 10$ ) conditions. Results for tests performed with the addition of 1 mg/L orthophosphate are not shown because they were similar to those shown in Figure 7, except that all of the NDMA concentrations were reduced. Generally, NDMA formation in each pipe loop increased with increasing HRT, as expected. Under turbulent conditions, the sequence of NDMA formation potentials in the four pipe loops followed the order of  $Cu \approx Pb < Fe < PVC$ , whereas chloramine decay constants followed the opposite order (Figure 5), which is in agreement

with common knowledge that chloramine presence is a rate-limiting factor for NDMA formation.

It was interesting to observe that changing flow conditions changed some of these relationships. NDMA concentrations were generally higher under laminar conditions than turbulent conditions and the pipe materials exhibited even more pronounced but different effects on NDMA formation. NDMA formation did not always directly correlate with chloramine presence. For example, although chloramine decay constants in the four pipe loops were statistically similar under this condition (Figure 5), the NDMA formation potentials followed a distinctly different sequence (an increasing order of Fe, Pb, PVC and Cu, as illustrated in Figure 7). In particular, the measured NDMA concentration in the copper loop tended to plateau at approximately 180 ng/L after 6 hours, but in the PVC loop (the control loop) there was only 65 ng/L NDMA at HRT of 6 hours and 150 ng/L NDMA present after 12 hours. Thus, the chloramine decay constants were comparable but NDMA formation was enhanced in the copper loop relative to the PVC loop, indicating that Cu(II) may have catalysed NDMA formation under laminar flow conditions.

In addition, for the iron loop, although chloramine degraded more quickly under turbulent conditions than under laminar flow (Figure 5 and Table 3), Figure 7 shows that NDMA yields after HRT 6 hours under turbulent conditions were at least 70% higher than those under laminar conditions. Catalytic effects of iron corrosion products during NDMA formation may, therefore, be suggested. In general, reactions mediated by surface-bound metal are affected by the mineral's surface area and the density of sorbed metal ions (Chun *et al.* 2005). The high velocity of turbulent water may enhance the release of iron corrosion

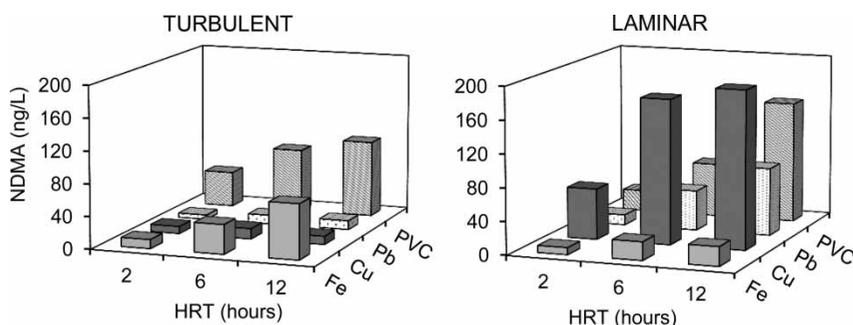


Figure 7 | NDMA formation in four pipe loops in the absence of orthophosphate under two flow conditions.

products from the pipe wall, thereby increasing the surface area of iron corrosion products in contact with DMA. As a consequence, NDMA formation was likely catalysed by iron corrosion products under turbulent flow in the current tests despite the relatively rapid chloramine degradation. These observations concerning the dependency of copper and iron influences on flow conditions have not been reported previously.

### Effects of orthophosphate

Since orthophosphate's corrosion preventive effects can generally reduce the impacts of the tested parameters on corrosion rates and metal concentrations, this study also investigated the effects of orthophosphate on NDMA formation.

NDMA concentrations in the tested loop effluents were normalized to those in the PVC control loop and are shown in Figure 8. Since the calculated relative percentage values of NDMA formation in the PVC loop were all 100%, they are not shown individually, but are indicated by the horizontal line at 100%. This normalization treatment of the data was necessary because partway through the experimental plan, the treatment plant performed some operational changes (increasing polyaluminium chloride, PACl) to improve their filter performance and, coincidentally, NDMA yields in the four pipe loops significantly decreased. Since the make-up and flow rate of the orthophosphate/DMA dosing solution and the flow rate of the reservoir effluent remained constant before and after the operational changes, the decreased NDMA formation was most likely attributable to changes in the organic characteristics of the

chloraminated reservoir water as a result of the increased PACl addition by removing some organic matter and/or changing its composition. Such effects of changing water matrix characteristics on NDMA formation have also been reported by Oya *et al.* (2008). Regardless, to account for variations in water quality, the effects of orthophosphate on NDMA formation were determined after first normalizing the NDMA concentrations in the different loops relative to those observed in the PVC control loop.

Under turbulent conditions, NDMA formation relative to the PVC loop in all three of the metal loops increased in the presence of orthophosphate compared with that in the absence of orthophosphate. The greatest increase was observed in the iron loop, in which more NDMA formed than in the PVC loop after the addition of orthophosphate. Recall that there was higher NDMA formation but more rapid chloramine decay in the iron loop under turbulent conditions than laminar conditions, suggesting the possible catalysis of iron on NDMA formation (see section on Effects of flow conditions). The additional evidence of increased NDMA formation after the addition of orthophosphate in the iron loop indicates that orthophosphate may significantly increase the catalytic effects of iron corrosion products, possibly by affecting the properties of iron particles and their suspension in the solution (Lytle & Snoeyink 2002). As for the copper and lead loops, recall that both chloramine decay and metal corrosion rates were significantly decreased in the presence of orthophosphate (Table 4). Since chloramine decay is a rate-limiting factor for NDMA formation and lower decay rates mean higher chloramine concentrations being present, it was also reasonable to have observed the increased formation

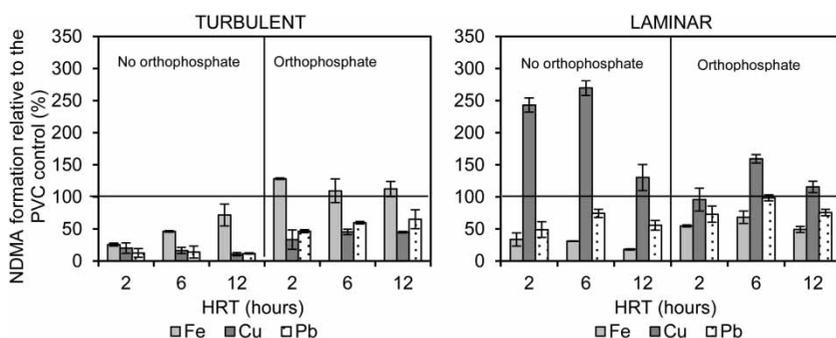


Figure 8 | NDMA formation relative to the PVC control in the absence and presence of 1 mg/L orthophosphate under laminar and turbulent flow conditions.

of NDMA in these two loops after the addition of orthophosphate.

Under laminar conditions, the main observation was that NDMA formation relative to the PVC control in the copper loop was significantly higher than 100%, especially in the absence of orthophosphate. This confirms the trends shown in Figure 7 that illustrate copper catalysis of NDMA formation under laminar conditions. Furthermore, the addition of orthophosphate decreased the percentage values of NDMA formation relative to the PVC control in the copper loop for all HRTs. Considering, too, the released copper concentration data from Figure 3, it is suggested that orthophosphate may mitigate both the copper catalysis of NDMA formation and copper corrosion.

## CONCLUSIONS

This study employed modified pipe loops to determine the effects of pipe materials, flow conditions and orthophosphate on chloramine decay and NDMA formation from DMA. Ductile iron, copper, lead and PVC were tested. Three flow regimes encountered in distribution systems (turbulent, laminar and stagnant) were examined. In general, the pipe materials, flow conditions and orthophosphate were all observed to influence metal corrosion, chloramine decay and NDMA formation as follows:

1. In agreement with previous studies, the released copper concentrations were reduced under laminar conditions and/or in the presence of orthophosphate. Decreased iron and lead concentrations were only observed under laminar conditions in the absence of orthophosphate. Lead release actually increased under laminar conditions in orthophosphate-treated water, along with a concurrent increase in nitrite concentration, suggesting the possible participation of nitrite as per previously reported lead corrosion reactions.
2. Chloramine degradation in the iron loop increased after the addition of orthophosphate regardless of flow conditions. Chloramine rapidly dissipated in the copper and lead loops under turbulent conditions in the absence of orthophosphate, but its degradation rate was decreased after the addition of orthophosphate.

3. Consistent with previous studies, chloramine concentration was generally a rate-limiting factor for NDMA formation, especially under turbulent conditions.
4. Regardless of the presence of orthophosphate, NDMA formation from DMA was significantly increased in the copper loop relative to the control loop under laminar conditions. A similar increase was observed in the iron loop but under turbulent conditions. Iron catalysis of NDMA formation became more prominent after the addition of orthophosphate possibly because orthophosphate modified properties of the associated suspended particles, whereas the decreased copper catalysis observed in the presence of orthophosphate was likely due to reduced dissolved copper concentrations.

Results of this study help in examining the complex reactions involving metal corrosion, chloramine degradation and NDMA formation under different flow conditions in distribution systems. Since it is an initial study that has identified the catalytic impacts of iron and copper on NDMA formation and their dependency on flow conditions, further study is recommended to investigate the mechanisms for iron and copper catalysis. Nevertheless, knowing more about impacts of pipe materials and corrosion inhibitors as well as the possible occurrence of nitrification on the stability of chloramine residuals and subsequent NDMA formation will be useful in developing strategies to control metal corrosion and reduce DBP formation in distribution systems.

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