The effect of zinc orthophosphate and pH–alkalinity adjustment on metal levels leached into drinking water

D.M. Churchill, D.S. Mavinic, D.G. Neden, and D.M. MacQuarrie

Abstract: A 12-month pilot plant study was conducted to evaluate a number of corrosion control treatments to reduce metal leaching from typical household plumbing materials. A pipe loop system was used to test six treatment options, with a control loop of the characteristically soft, acidic, Greater Vancouver Water District (GVWD) water. Four pH–alkalinity combinations and two concentrations of zinc orthophosphate (0.37 mg/L and 1.0 mg/L as Zn) were studied. at regular intervals, the flowing, treated, and control waters were allowed to stagnate in the pipe loop system for 8- and 16-h periods. Following the designated standing time, water samples taken from the lead/tin solder jointed, soft copper plumbing coils, the submerged, free standing coils of 50/50 lead/tin solder, and the brass faucets, were measured for lead, copper, and zinc levels. Overall, when compared to the control loop, the pH–alkalinity treatments appeared to exacerbate metal leaching in standing samples. The zinc orthophosphate treated loops were both effective at reducing lead and copper leaching to below control levels. In general, the two standing times showed little difference in the levels of leached metals. The exception to this occurred in the higher dose zinc orthophosphate loop, which had higher copper and zinc levels at the longer standing time.

Key words: copper, corrosion, drinking water, lead, zinc orthophosphate.

Résumé : Une étude pilote de 12 mois d'une installation à été effectuée afin d'évaluer plusieurs traitements pour contrôler la corrosion et réduire la corrosion de matériaux de plomberie domestique typiques. Une boucle de tuyaux a été testée en utilisant six options de traitement, avec une boucle de contrôle contenant de l'eau au caractère doux et acide du Greater Vancouver Water District (GVWD). Quatre combinaisons pH–alcalinité et deux concentrations d'orthophosphate de zinc (0,37 mg/L et 1,0 mg/L en forme de Zn) ont été étudiées. À intervalles réguliers, l'écoulement des eaux traitées et de contrôle a été arrêté pour que l'eau stagne dans la boucle de tuyaux pendant une période de 8 et 16 h. Après une période de stagnation désignée des échantillons d'eau étaient pris à partir du serpentin de plomberie en cuivre tendre, joints par des soudures plomb/étain; des serpentins submergés autoportants aux soudures 50/50 plomb/étain; et des robinets en laiton. Les concentrations de plomb, cuivre et zinc ont étés mesurées. Dans l'ensemble, comparé à la boucle de contrôle, les traitements de pH–alcalinité semblaient exacerber la corrosion des métaux dans les échantillons stagnants. Les boucles traitées à l'orthophosphate de zinc étaient efficaces pour la réduction de la corrosion du plomb et du cuivre en dessous de niveaux de contrôle. En général, les deux durées de stagnation ont présentées peu de différences dans les niveaux de métaux. La seule exception était la boucle à dosage plus élevé d'orthophosphate de zinc, qui présentait des niveaux plus élevés de cuivre et de zinc pour les durées de stagnation plus longues.

Mots clés : cuivre, corrosion, eau potable, plomb, orthophosphate de zinc.

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Introduction

Background

The Greater Vancouver Water District (GVWD) provides water for approximately 1.8 million people in 18 communities in the lower mainland of British Columbia. Water supplied from GVWD's three surface water impoundments is of high quality. Chlorine disinfection and course screening are the only treatments currently practised.

The geological and geographical characteristics of the Coast Mountains, in which the water catchment areas are located, have an important effect on the water quality, leading to source waters that are of low pH, alkalinity, and hardness. These and other characteristics, such as high dissolved oxy-

Table 1. GVWD source water quality characteristics.*

Corrosive characteristics	Parameters measured	Typical values
Low pH	pH	6.0–6.3
Low alkalinity (poor buffering capacity)	Total alkalinity as $CaCO_3$	1.5–3.7 mg/L
Low hardness	Hardness as $CaCO_3$	3.21–5.10 mg/L
High dissolved oxygen levels	Dissolved oxygen	8.1–12.8 mg/L
Low mineral content	Calcium	1.08–1.76 mg/L
	Magnesium	0.13–0.17 mg/L
Low dissolved solids	Total l	12–16 mg/L

*Data from EES (1990).

gen levels, low mineral content, and low dissolved solids (see Table 1), cause the waters to be highly corrosive to unlined metal piping of drinking water distribution systems.

Corrosion impacts

Water of low pH and low alkalinity is unable to form a protective film of calcium carbonate on the surface of piping systems. High, uniform corrosion rates are most commonly associated with these types of waters. This can lead to unacceptable levels of corrosion by-products, such as copper and lead, being introduced into drinking water, which in turn can have deleterious effects on human health. Increasing awareness of the presence and potential health impacts of corrosion products in drinking water has led the US Environmental Protection Agency to mandate action levels of 0.015 mg/L for lead and 1.3 mg/L for copper (Pontius 1991). Canadian drinking water guideline levels (Health and Welfare Canada 1996) are 0.01 mg/L maximum acceptable concentration (MAC) for lead, on a flushed sample, and ≤1.0 mg/L aesthetic objective (AO) for copper.

Corrosion can also have negative impacts on the environment. Copper and zinc are toxic to fish and microorganisms at quite low concentrations and may pose a threat to receiving waters and sewage treatment plants. Corrosion leads to premature failure of plumbing and piping systems and can cause problems such as metallic tasting water and staining of plumbing fixtures, clothing, and human hair.

Household plumbing

Corrosion in the GVWD service area is primarily a problem in household and building piping systems, since these systems are unlined; in addition, unlike most distribution mains, they frequently have large sections of piping in which water can be stagnant for hours. Copper plumbing with lead/tin solder (which was widely used until 1989) and brass faucets predominate in household plumbing systems.

Lead/tin solder (50% lead/50% tin) is of particular concern when considering the leaching of lead, because the electrochemical nature of the solder–copper couple creates a galvanic cell. The more noble copper serves as the cathode (area for electron consumption reaction), while the more electronegative solder serves as the anode (oxidation site) and the point of metal release. Lead-based solder has been found to be the most significant source of lead at the tap (Lee et al. 1989; Schock and Wagner 1985).

Brass faucets (containing 2–8% lead) with chrome plated exteriors are used almost universally for kitchen and bathroom sinks. Studies show that faucets, brass valves, and fittings can be a significant source of lead and zinc contami-

nation of drinking water (Schock and Neff 1988; Samuels and Meranger 1984; Mattson 1980). Lee et al. (1989) found that brass faucets contributed an average of one third of the lead in 1 L, first draw, standing samples.
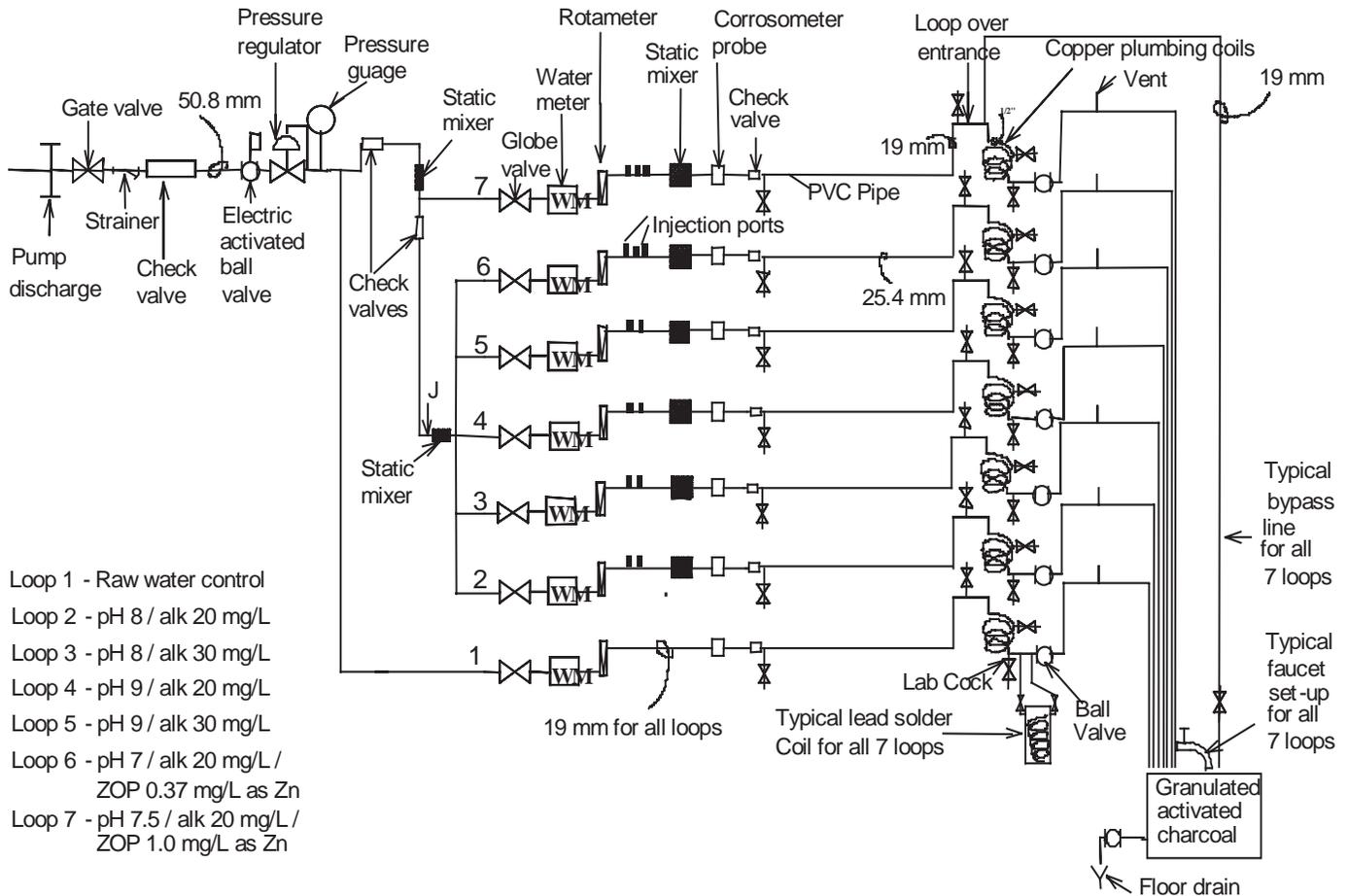
Previous studies/objectives

As part of the GVWD Corrosion Control Initiative, a 1988–1990 pilot scale study was undertaken by Economic and Engineering Services (EES) of Olympia, Wash. (EES 1990). This study concluded that disinfecting with chloramine instead of chlorine and adjusting pH and alkalinity to 8–8.5 and 20 mg/L as $CaCO_3$, respectively, could reduce copper corrosion by 60–80% and lead corrosion by 10–60% over corrosion levels of the normal, chlorinated water currently produced by the GVWD. That study also recommended further pilot testing to examine chemical inhibitors as an adjunct to pH and alkalinity adjustment.

In a follow-up study (MacQuarrie et al. 1997), the chemical corrosion inhibitors zinc orthophosphate, type N sodium silicate, and a commercial blend of the two were studied in water with adjusted pH and alkalinity and disinfected with chloramine. That study measured corrosion using pipe coupon inserts and corrosometer probes. The results of the weight loss determinations from the pipe inserts indicated that all of the inhibitors, particularly the zinc orthophosphate, worked very favourably with copper; however, for cast iron coupons, it offered no additional benefit over that obtained from simple pH and alkalinity adjustment. The metal leaching results, however, showed some very high metal levels from some of the inhibitor loops. Further study was recommended with zinc orthophosphate and its effect on metal leaching and the relation of metal leaching to length of standing time, pH, and alkalinity fluctuations.

Recommendations from these studies, in addition to drinking water standards and health concerns that are based on actual metal levels in drinking water (rather than corrosion rates), led to the investigations discussed in this paper. The main purpose of this study was to evaluate various applications of corrosion control methods for drinking water. The levels of metals leached from typical household plumbing materials, which were exposed to these control methods, were measured, to compare the effectiveness of the different methods in reducing lead, copper, and zinc levels in the water.

Solubilities of the various metals in a water system are influenced by many ion pairs and complexes. Alkalinity and pH have been found to have a strong effect on the solubility of lead and copper (Schock 1989; Edwards et al. 1994; Vinci and Sarapata 1992). Zinc solubility is less influenced by

Fig. 1. Seymour Dam pilot plant schematic.

Loop 1 - Raw water control
Loop 2 - pH 8 / alk 20 mg/L
Loop 3 - pH 8 / alk 30 mg/L
Loop 4 - pH 9 / alk 20 mg/L
Loop 5 - pH 9 / alk 30 mg/L
Loop 6 - pH 7 / alk 20 mg/L /
        ZOP 0.37 mg/L as Zn
Loop 7 - pH 7.5 / alk 20 mg/L /
        ZOP 1.0 mg/L as Zn

pH (Stone et al. 1987). Solubility theory indicates the minimum lead solubility point is at a pH of 9.8 and a total alkalinity of about 28 mg/L as $CaCO_3$ (Schock 1989). Copper solubility is lowest in the pH range of 8.5 to 9 at alkalinities of 20 to 30 mg/L as $CaCO_3$ (Vinci and Sarapata 1992).

Experimental methods

Selection of inhibitors

In low pH, low alkalinity, and low hardness water, increasing its pH has been shown to be very important in reducing corrosivity of water, particularly to copper and lead. An increase in pH reduces the solubility of metals and of the protective metal oxide film and interferes with corrosion cell reactions. In general, pH values ≥ 8 provide best control for copper and lead corrosion (Edwards et al. 1994; Lee et al. 1989).

In hard water, adjusting water quality parameters such as pH is used to promote precipitation of calcium carbonate to form a protective scale. In soft water, however, the water is not saturated enough with calcium carbonate to form this protective film. It is not practical in the low pH, low alkalinity waters of the GVWD to achieve, by water quality adjustment, the levels of calcium and carbonate alkalinity necessary for calcium carbonate precipitation and scale protection. Increasing alkalinity, however, can provide buffer capacity to maintain pH stability. In addition, it will add bicarbonate

and carbonates, which have been shown to have beneficial effects, even at levels below that required for calcium carbonate precipitation, in corrosion control (Johnson et al. 1993; Judge 1994; Vinci and Sarapata 1992).

Numerous studies have demonstrated mixed results with chemical corrosion inhibitors. The literature generally suggests that the effectiveness of phosphates as corrosion inhibitors, is limited to iron and lead surfaces. However, Reiber (1989) found orthophosphates to significantly reduce corrosion rates on copper surfaces. A previous study at the GVWD's Seymour Dam pilot plant found that copper coupon corrosion rates for the zinc orthophosphate loops showed a 77% improvement over that of raw water (MacQuarrie et al. 1997).

Pipe loop configuration

This study was conducted under pilot plant conditions, using a pipe loop system located at the GVWD's Seymour Falls Dam (Fig. 1). Alternative treatment approaches were studied to compare their relative effectiveness. The treatment options investigated were pH–alkalinity adjustment and the chemical corrosion inhibitor, zinc orthophosphate. The effects of 8- and 16-h water-sample standing times on metal levels for the various treatment options were also compared.

Four pH–alkalinity combinations and two different concentrations of zinc orthophosphate (ZOP) were evaluated (Table 2). The pH was raised by addition of lime $(Ca(OH)_2)$

Table 2. Target treatment values.

Loop number	pH	Alkalinity (mg/L as CaCO$_3$)	Zinc orthophosphate (mg/L as Zn)
1	Raw water control	Raw water control	—
2	8	20	—
3	8	30	—
4	9	20	—
5	9	30	—
6	7	20	0.37
7	7.5	20	1.0

and alkalinity was raised by addition of sodium bicarbonate (NaHCO$_3$). The zinc orthophosphate used was a commercial preparation from Technical Products Corp. (TPC) of Portsmouth, Va., called Virchem 939. It comes in liquid form with a zinc content of 8.3% and a zinc-to-phosphate ratio of 1:3.

Prior to commencement of the study, the loops to be treated were flushed with an acidic solution to dissolve scale that may have built up from previous studies. Following subsequent flushing of all the loops with raw source water for 11 days, the loops used for zinc orthophosphate treatment, Loops 6 and 7, were passivated prior to beginning treatment by running zinc orthophosphate for 10 days at a high dose (1.5 mg/L as Zn). Target treatment values are given in Table 2.

Pilot plant design

The pilot plant was located at Seymour Falls Dam, at the base of Seymour Lake, the raw water source for the study. Water pressure was reduced and regulated to provide constant pressure to the pilot plant. In order to create a flow velocity through the copper plumbing coils of the pipe loop system similar to that in household plumbing and the same as that used in previous GVWD studies, globe valves were used to regulate flow through the coils to 0.79 m/s (2.6 fps). Water flow was controlled by an electrically operated ball valve and an electronic timer commenced and shut down flow of water and chemicals. Water flowed for a total of 6 h each day through the system, resulting in 2166 L (573 US gal) per day through each pipe loop.

The pipe loop system (Fig. 1) consisted of seven parallel, pipe loop sets that operated simultaneously. A chemical feed system delivered the specified chemicals, via Norprene tubing and variable speed Masterflex peristaltic pumps, to injection ports on each pipe loop set. In-line static mixers to ensure rapid mixing followed these ports. This system allowed for six treatment options and one control loop to be evaluated throughout the 12-month study.

Each of the seven loops contained three sections in which water could be isolated and allowed to remain stagnant for the desired standing time, after which samples could be drawn from each section to measure the levels of leached metals. The first section, following the chemical injection ports and static mixers, was a 25.6-m (84-foot) coil of half inch soft copper plumbing, joined every 1.22 m (4 feet) with 50/50 lead/tin solder. Immediately downstream, on each loop, the water flowed through a plastic canister holding a freestanding coil of 50/50 lead/tin solder material. The outlet of each loop was a two-handled, cast brass mixing faucet.

The plumbing coils and faucets were intended to simulate metal leaching from typical household plumbing materials. Lead concentrations found in the solder coil samples were used to indicate the relative lead solubility that resulted from the different treatments.

Sampling and analysis

Prior to sampling, the flowing, raw water and treated water were isolated in each section of each pipe loop and then left to stagnate for the designated standing time. Initially, an 8-h standing time was used. After 7 months of the 12-month study, on alternate weeks, 16-h samples were also drawn, thus allowing comparison between two different standing times.

At approximately 3-week intervals, water samples were drawn, after the appropriate standing time, from each section on all seven loops: two 500-mL samples from each plumbing coil, one 500-mL sample from each solder coil canister, and one 250-mL sample from each faucet. The samples were immediately preserved with nitric acid and were brought to the University of British Columbia Environmental Laboratory, Department of Civil Engineering, for acid digestion. Each sample was analysed for lead, copper, and zinc.

Copper, zinc, and the higher level lead samples from the solder coils were analysed using a Thermo Jarrel Ash Atomic Absorption Spectrophotometer, (with detection limits of 0.01 mg/L for copper, 0.005 mg/L for zinc, and 0.05 mg/L for lead). The low-level lead samples were measured on a Perkin-Elmer, HGA-500 graphite-furnace Atomic Absorption Spectrophotometer (with a lead detection limit of 0.001 mg/L).

Results and discussion

Statistical analyses included determination of averages, standard deviations, and confidence intervals, for each series of data. Statistical significance was determined using a one-tailed, Student's t-test. If the observed significance level, or probability (P value) was less than 5% ($P = <0.05$), the result was considered statistically significant. If the probability was less than 1% ($P = <0.01$), the result was considered statistically, highly significant.
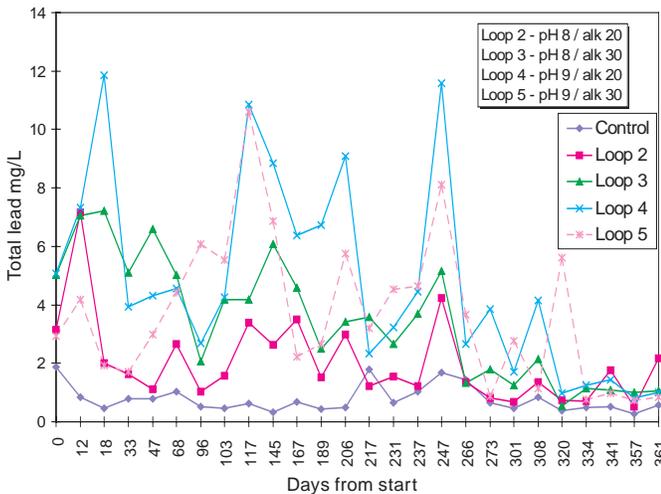
Lead concentrations in standing water samples

The measured lead levels and the average lead levels, are represented graphically in Figs. 2 to 5. The following observations were made from the data and graphs.

Fig. 2. Solder coils – average lead levels: 8- and 16-h samples.
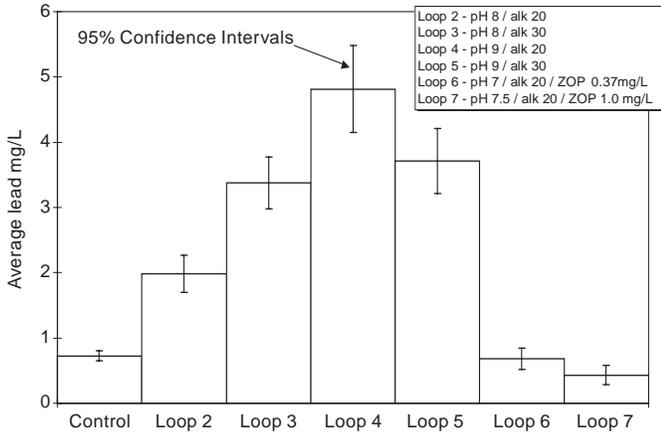
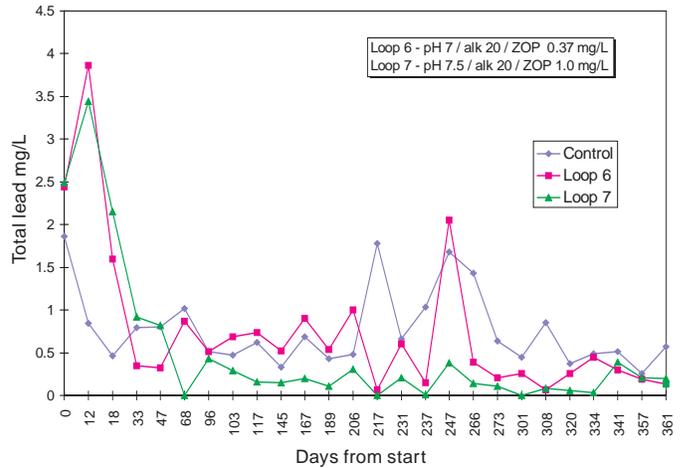**Fig. 3.** Solder coils – measured lead levels: pH–alkalinity adjusted loops: 8- and 16-h samples.

Fig. 4. Solder coils – measured lead levels: ZOP treated loops: 8- and 16-h samples.

Fig. 5. Decline in lead levels over time: solder coils – average lead levels at 0–4, 4–8, and 8–12 months.

Lead in solder coil standing water samples

From Fig. 2, it would appear that all pH–alkalinity treatments exacerbated lead leaching. The average concentrations for all pH–alkalinity treated loops were significantly higher than the control. Measured lead levels for these loops are highly variable, as seen in Fig. 3, especially for Loop 4, which had spikes of lead concentrations up to 12 mg/L. Loop 4, which was adjusted to pH 9, had significantly higher average lead levels than Loops 2 and 3, which were adjusted to pH 8. These results are surprising, considering that minimum lead solubility normally occurs at pH values in excess of pH 8.5.

In this case, it may not be useful to compare the lead levels from the treated loops to the control loop, since the treated loops were acidified before commencing this study. Loop 1 had been the control loop in all studies conducted and received no treatment or chemical injection. This factor may have resulted in the control loop having an aged surface and the treated loops a fresher surface. A new surface is known to corrode faster than an aged surface and to be more sensitive to changes in pH, for lead/tin solder (Reiber 1991).

Figures 2 and 4 show that the ZOP loops consistently produced the lowest lead concentrations, significantly below the lead levels in the pH–alkalinity adjusted loops, and with much less spiking of lead levels. However, when compared to the control loop, the difference in the overall average lead levels is not statistically significant.

Figure 5 demonstrates the decrease in average lead levels in the last 4 months of the study, for all treated loops. The observed significance level for the difference in average lead levels at 0–4 months and 8–12 months was less than 5% for all treated loops and thus indicates that the decrease was statistically significant. In addition, when data for the last 4 months from both ZOP loops are compared to the control loop, the ZOP lead levels are highly significantly less than the control.

Lead in plumbing coil and faucet standing water samples

The lead concentrations from all the plumbing coils were extremely low, possibly due to depletion of leachable metal from previous studies.

Lead concentrations from the faucets were also quite low; however, all treated loops had highly significantly lower average lead levels than the control loop.

Fig. 6. Plumbing coils – average copper levels: 8- and 16-h samples.

Fig. 7. Plumbing coils – measured copper levels: pH–alkalinity adjusted loops: 8- and 16-h samples.
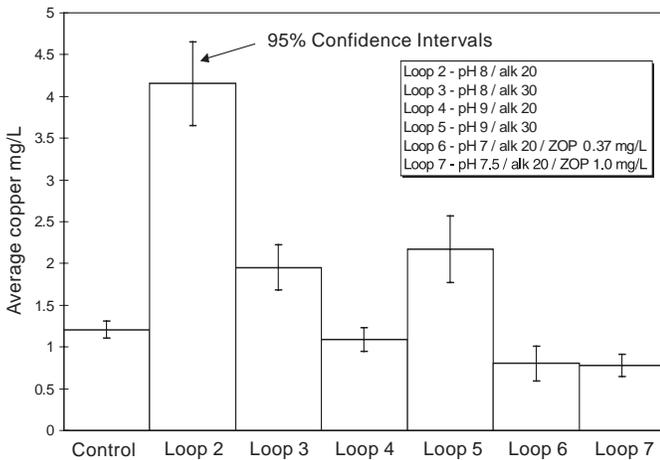
Copper in standing water samples

The measured copper levels and the average copper levels in each loop are represented graphically in Figs. 6 to 10. The following observations are made from the data and graphs.

Copper in copper plumbing coil standing water samples

Figure 6 indicates that Loops 6 and 7, the zinc ortho-phosphate loops, achieved the lowest average copper levels in the plumbing coils. For Loop 6, relative to the control loop, the difference is not significant; however, for Loop 7 the difference is considered statistically significant.

Loop 4 was the only pH–alkalinity loop that had any reduction in average copper concentration from its pretreatment level. However, when compared to the control, the difference in average concentrations was not statistically significant. The remaining pH–alkalinity loops appeared to exacerbate copper leaching to well above pretreatment levels and above the control loop level.

Figure 7 shows that some high copper levels were encountered. The highest levels were from Loop 2, which had an average copper level of 4.15 mg/L, well above the 1.25 mg/L average for the control loop. All loops, except the control loop, periodically experienced high concentrations in the form of spikes. The spikes occurred less frequently and were of lower concentrations in the ZOP loops (Fig. 8).
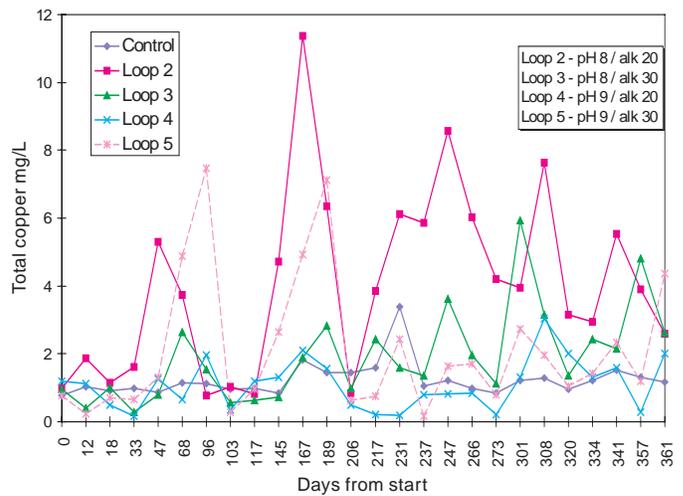
Copper in faucet standing water samples

The copper found in faucet standing water samples would be the combined contributions of background copper in the flowing waters from the upstream, copper plumbing coils and the copper leached from the faucets while standing. The brass faucets appeared to respond much better to the treated waters than did the copper plumbing coils. The average copper levels for all treated loops were significantly below that of the untreated control loop (Fig. 9). Similar to the plumbing coils, Loop 4 had the lowest average copper concentration.

Copper in solder coil standing water samples

The copper measured from the solder coil standing water samples originated from background copper in the flowing water from the upstream, copper plumbing coils. The average copper levels in the treated loops were all significantly below that of the control loop (Fig. 10). This may indicate that all the treated waters provided some beneficial effect at reducing copper levels, under flowing conditions. Again, Loop 4 had the lowest average copper level. The zinc ortho-phosphate loops did not appear to provide any better protection than the pH–alkalinity loops.

Zinc in standing water samples

Zinc levels are represented graphically in Figs. 11 and 12. The following observations are made from the data and graphs.

Among the plumbing materials tested, brass faucets provided the highest source of zinc. Again, the faucets appeared to respond well to treatment. The faucets from all the pH–alkalinity treated loops had average zinc levels significantly below the control average.

Figure 11 compares average zinc levels, for Loops 6 and 7, from the plumbing coil, solder coil, and faucet standing water samples. For the faucets and solder coils, and the plumbing coil of Loop 6, the average level of zinc is somewhat higher, but roughly approximates, the feed rate of zinc to those loops (0.37 mg/L to Loop 6 and 1.0 mg/L to Loop 7). However, the plumbing coil of Loop 7 had an average zinc concentration more than double that of the feed rate.

Figure 12 graphically demonstrates the measured zinc concentrations in the plumbing coils for Loops 6 and 7 over the term of the study. As shown, Loop 7 frequently had high concentrations of zinc in the form of spikes. In Loop 6, the concentrations were much more stable and, as shown in Fig. 11, average concentrations were similar to those found in the faucets and solder coils. Since the plumbing coils are upstream of the brass faucets, the only likely source for the high zinc levels is the zinc orthophosphate itself.
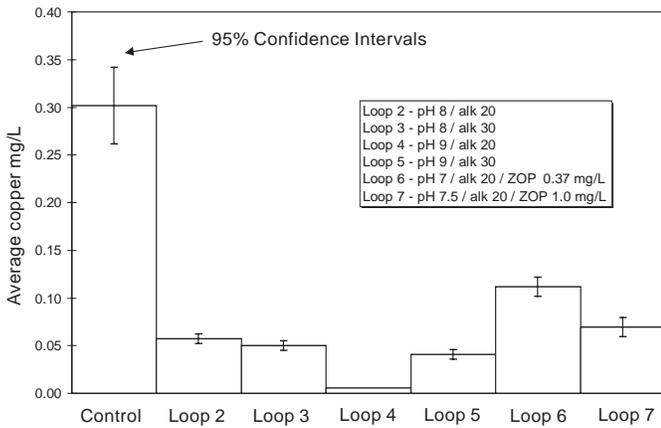
Comparison of 8- and 16-h standing times

Metal levels in 8- and 16-h standing water samples are compared graphically in Figs. 13 to 16. The following observations are made from the data and graphs.
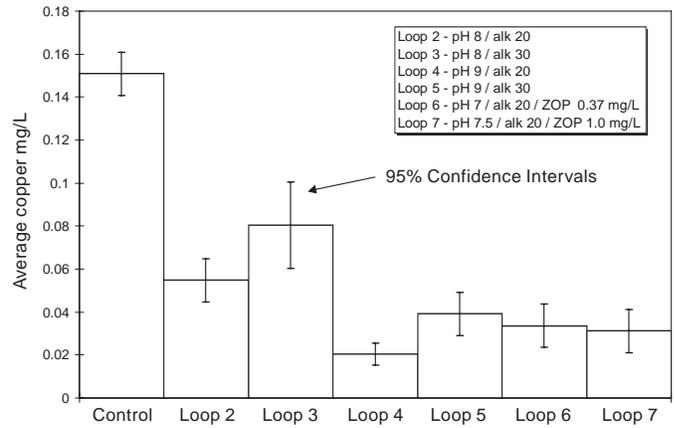
Fig. 8. Plumbing coils – measured copper levels: ZOP treated loops: 8- and 16-h samples.
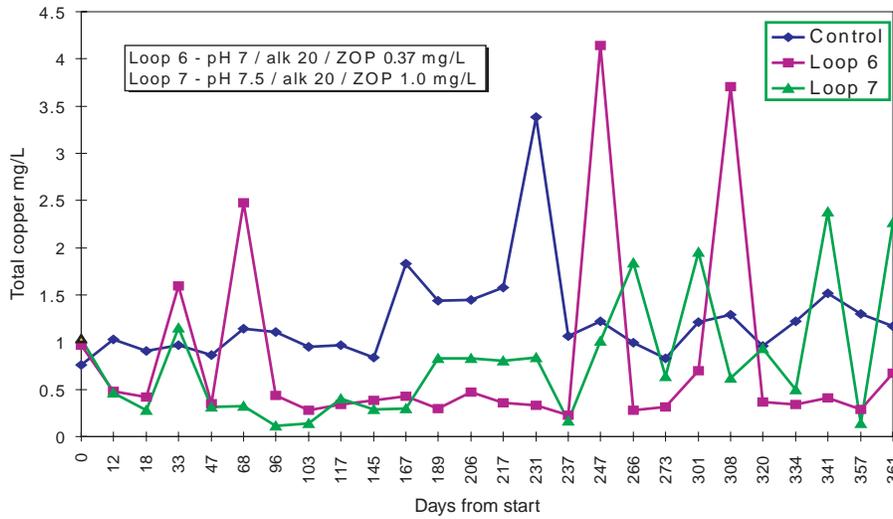
Fig. 9. Faucets – average copper levels: 8- and 16-h samples.

Fig. 10. Solder coils – average copper levels: 8- and 16-h samples.

Eight and sixteen-hour lead levels

Figure 13 compares average lead levels at 8- and 16-h standing times. Statistically, there was no significant difference between the two standing times for any of the loops. Lee et al. (1989), in measuring lead at the tap from lead service pipes, found that the largest increment of lead increase occurred in the first 2 h, but continued to increase for up to 6 h (and sometimes longer). It is likely in this study, after 8 h of standing, the majority of the leaching had occurred. Zinc orthophosphate, which is considered to be less effective under long standing time conditions, was in this case just as effective after 16 h as it was after 8 h.

Eight and sixteen-hour copper levels

Copper levels in the pH–alkalinity loops did not, overall, appear to be affected by the longer standing time (Fig. 14). Only Loop 3 had levels of copper, at the longer standing time, which were significantly higher.

The 16-h samples from Loop 7 of the plumbing coils (Fig. 14) had an average copper concentration more than three times as compared to the 8-h samples, a difference that is statistically highly significant. This may indicate a re-

duced effectiveness of zinc orthophosphate for copper corrosion after longer stagnation periods.

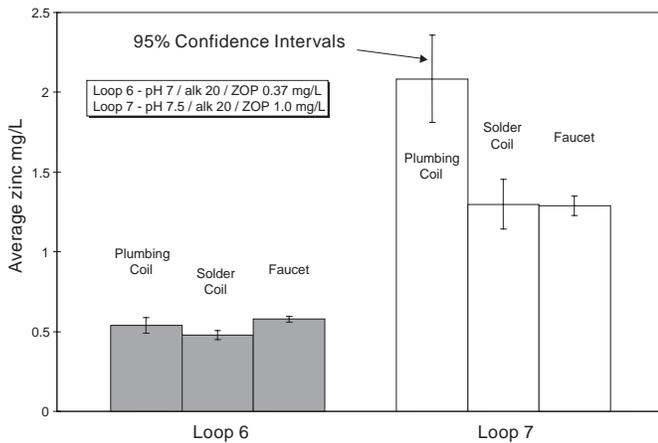Copper levels in the faucets were not affected by the longer standing time.

Eight- and sixteen-hour zinc levels

Figure 15 compares average zinc levels from Loops 6 and 7 faucets, at 8- and 16-h standing times. Again, Loop 7 had a significantly higher average metal concentration after the longer standing time. In Fig. 16, average zinc levels from the plumbing coils are compared at the two standing times. The Loop 7 zinc level after the longer standing time was also significantly higher. The consistently higher levels for copper and zinc in Loop 7 after 16 h standing indicate that the higher dose of zinc orthophosphate may be affected by standing time.
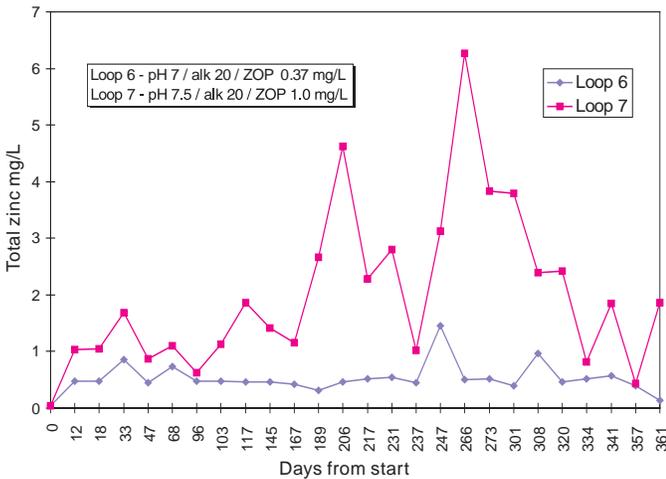
Summary

The main objective of this study was to determine which of the tested corrosion control techniques would most effectively reduce lead and copper concentrations in drinking water from household piping and plumbing. Although a pipe

Fig. 11. Average zinc levels – ZOP treated loops: 8- and 16-h samples.

Fig. 13. Solder coils – average lead levels: 8- vs. 16-h standing water samples.

Fig. 12. Plumbing coils – measured zinc levels: ZOP treated loops: 8- and 16-h samples.

higher dose ZOP loop had highly significantly less average lead than the control, and after 8 months of treatment the difference was highly significant for the lower dose as well.

Average copper levels from the plumbing coils of the ZOP loops were lower than the control; however, for Loop 6, the difference was not significant. For Loop 7, the difference was considered statistically significant. The ZOP loops experienced more frequent spiking of copper levels than they did with lead; the spiking of copper occurred most often in the last 4 months of the study and occurred more frequently for Loop 7.

The higher dose of ZOP (Loop 7) showed the more significant reduction in lead and copper; however, it also produced problems with spiking of copper and zinc. The plumbing coil of Loop 7 had spikes of zinc up to 6 mg/L, much higher than the feed rate of 1.0 mg/L ZOP as Zn. The high concentrations of zinc in the standing water samples, from the higher dose ZOP loop, are possibly caused by the inhibitor precipitating out before forming a protective scale; alternatively, the already-formed scale could be sloughing off.

These processes may be related to pH, alkalinity, and (or) the dose of inhibitor. For example, Loop 7 had a higher adjusted pH (pH 7.5) than did Loop 6 (pH 7.0). It has been found that, as orthophosphate dosage is increased, the optimum pH slowly decreases (Schock 1989). Technical Products Corporation, the manufacturer of Virchem 939, the ZOP formulation used in the study, has stated that as the pH approaches 8.5 ZOP comes out of solution, reducing its effectiveness (Technical Products Corporation 1992). In these waters, ZOP may have been sensitive to changes in pH and alkalinity. In addition there may be a narrow range of effective dose for ZOP and the dose may need to be adjusted, as necessary, when conditions change.

Zinc orthophosphate in the distribution system may effectively reduce metal levels. In addition, zinc is not considered a health concern (Canadian drinking water guidelines set an aesthetic objective level of ≤5.0 mg/L). Zinc is an essential nutrient and also provides some protective action against toxic metals such as cadmium and lead (National Academy of Science 1980). However, there are other impacts that must be considered. With the use of zinc orthophosphate, there is potential for elevated zinc levels, which would be
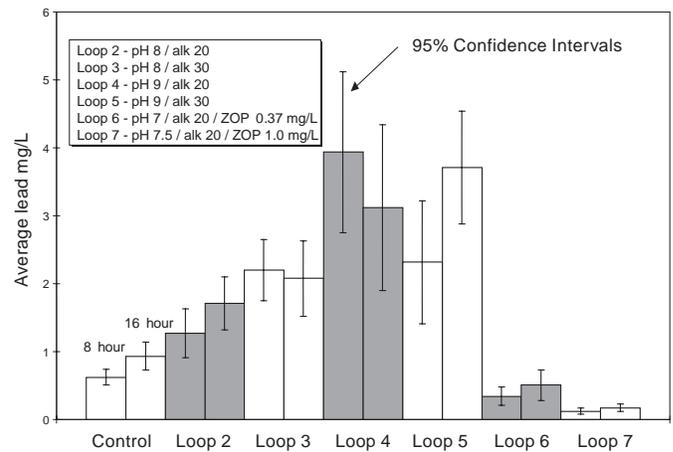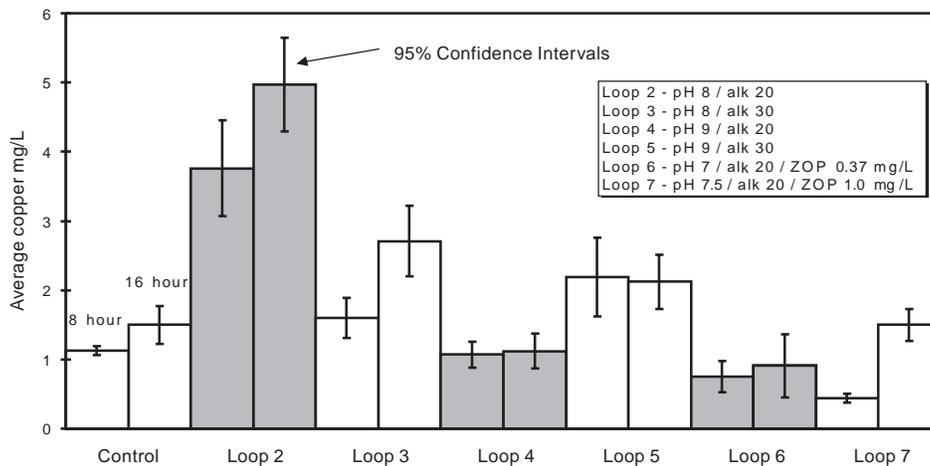
loop study allows testing with actual raw water and the types of materials that are used in household plumbing, the metal levels obtained will not directly equate with those that could be found in the actual distribution system. In addition, it cannot predict how effective the treatments will be in meeting the recommended lead and copper levels at the tap. However, this type of study can provide information on the relative effectiveness of various treatments for corrosion control, an important consideration if large-scale application to a major distribution network is being planned.

Zinc orthophosphate treatment

Overall, the zinc orthophosphate (ZOP) corrosion inhibitor provided the most effective treatment for reducing copper and lead concentrations in standing water samples. Compared to the pH–alkalinity loops, the ZOP loops consistently had significantly lower average metal levels, the most stable concentrations, and experienced less spiking of metal concentrations.

Compared to the control loop, the overall average lead levels from the solder coils of the ZOP loops were not significantly less. However, after 4 months of treatment the
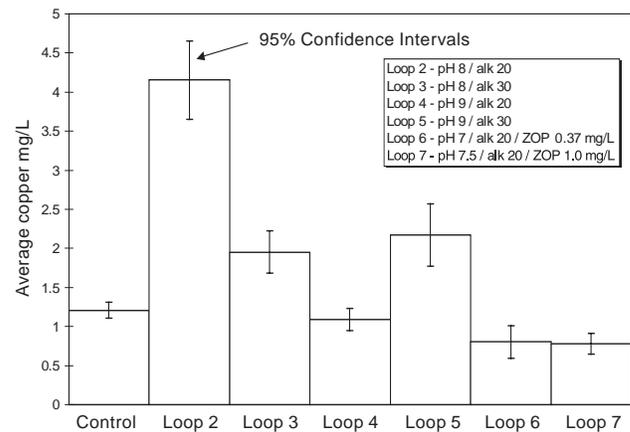
Fig. 14. Plumbing coils – average copper levels: 8- vs. 16-h standing water samples.

Fig. 15. ZOP faucets – average zinc levels: 8- vs. 16-h standing water samples.
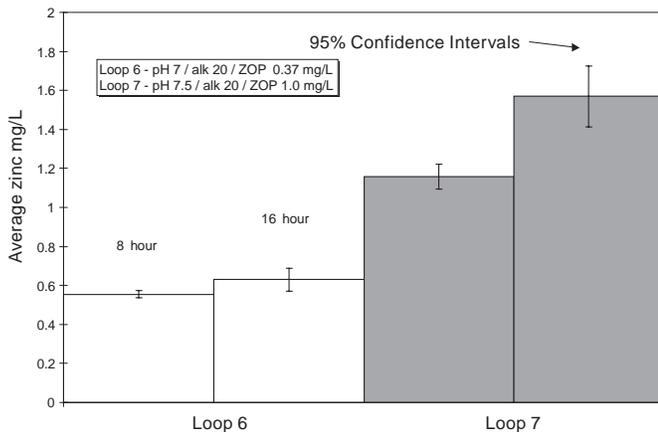
Fig. 16. ZOP plumbing coils – average zinc levels: 8- vs. 16-h standing water samples.

problematic for local wastewater treatment plants, especially in the management of sewage sludge. Zinc is also toxic to fish and so any additional zinc going into receiving waters must be monitored carefully. Phosphorus is an essential nutrient for microorganisms, so additional phosphorus from the zinc orthophosphate may also exacerbate bacterial regrowth problems in the distribution system. An increase in phosphorus content of discharged wastewater could also increase the risk of eutrophication of receiving waters, unless specific remedial action was in place.

pH–alkalinity treatment

The pH–alkalinity treatments generally appeared to exacerbate metal leaching in standing water samples. Of the four pH–alkalinity combinations tested, no one combination could be identified that provided the best overall reduction in metal levels. Average copper and lead levels in the pH–alkalinity loops were, for the most part, higher than the control levels. It appears that the scale that forms under these conditions on a fresh pipe surface is not as stable as the metal oxide scale that likely was present in the control loop. The concurrent, high standard deviations for pH and alkalinity that occurred in the treated loops may indicate that the treated loops were more sensitive to the variations in

pH than to the pH value itself. Reiber (1989) found that fresh copper surfaces were highly sensitive to pH. Johnson et al. (1993) concluded that a steady pH was probably the most important factor in achieving consistent corrosion control results.

The exception to these results occurred in the faucets. In the pH–alkalinity loop faucets all average metal levels were significantly less than the control loop.

There was a decline in lead levels, over time, for all loops, which may show benefits for pH–alkalinity treatment in the field, over the long term.

Standing time effects

For the most part, there was little difference in metal levels at the two standing times. The pH–alkalinity loops had similar results at 8- and 16-h standing times, as did Loop 6. The exception occurred in the higher dose ZOP loop (Loop 7), which had significantly higher average copper and zinc concentrations at the longer standing time. However, this was not the case for lead, which had similar levels at the two standing times in Loop 7.

Although metal levels in flowing water samples were not directly measured, the results from the solder coils and faucets give some indication of the metal levels that would oc-

cur under flowing conditions. Johnson et al. (1993) concluded that apparently there was a difference in the chemistry of corrosion control between flowing and standing conditions. This variation was evidenced by fluctuations in pH for standing water as compared to flowing water and also the effectiveness of pH–alkalinity treatment in decreasing copper concentration flowing water. This study produced similar results. The copper levels in the treated solder coil and faucet samples, which received flowing water from the upstream copper plumbing coils, were all significantly below the control loop, even for pH–alkalinity treatment. The same was true for lead in the faucets, which received flowing water from the upstream solder coils. Under these circumstances, the pH–alkalinity treatments were just as effective as zinc orthophosphate.

Overview

Although pH–alkalinity treatment was not very effective under pilot plant conditions, there may be benefits to the use of pH–alkalinity adjustment in the field. The pH–alkalinity treatment used in this study had some positive effects. It was effective at reducing metal levels in both the faucets and under flowing water conditions. The pH–alkalinity adjustment is relatively inexpensive and has been proven to work in many field studies as well as in actual distribution systems. Pilot plant results do not always reflect how a particular treatment will respond in a field distribution system in the long term. It must by kept in mind that, in this study, the pH–alkalinity treatments were applied to a fresh copper surface, because of flushing of the system with acid before starting the study. This type of surface is known to be more sensitive to pH and to variations in pH. In the field, one would more likely encounter aged plumbing surfaces.

This study also suggests that maintenance of a stable pH is important in reducing metal levels. Maintaining a stable pH, at a lower value, may prove to be easier, since at pH 7 there is a much higher buffer intensity than at pH 8 or 9 for the bicarbonate buffering system. In addition, the lower pH may be more beneficial for other water treatment considerations. For example, higher pH levels may make free chlorine less effective for use as a primary disinfectant, and raising pH, if done in the presence of chlorine, may increase the formation of trihalomethanes and increase the tendency of naturally occurring iron to precipitate.

Given the concerns with zinc orthophosphate, and its additional cost, it is recommended that pH–alkalinity adjustment be tried first in the GVWD member and municipality distribution systems to determine its overall effects. At the same time, further studies of zinc and non-zinc orthophosphate inhibitors may be undertaken at the pilot scale level or even in an isolated, small distribution system.

Conclusions

The results of this pilot scale water distribution study have brought to light a number of interesting and important observations and conclusions, with respect to the Greater Vancouver water distribution system. These are presented in no particular order.

The pH–alkalinity treatment was not very effective at reducing metal levels below those of the control in standing water samples. In comparing the pH–alkalinity loops, it was not possible to identify an "optimum" pH–alkalinity combination that was effective at reducing overall metal levels. However, pH–alkalinity treatment provided some corrosion protection under actual water flowing conditions.

Lead concentrations decreased dramatically in all pH–alkalinity loops in the last 4 months of the 12-month study period. This did not occur in the control loop. This indicates that pH–alkalinity treatment may provide some benefit to the distribution system in the long term.

Zinc orthophosphate (ZOP) was effective at reducing lead as well as copper concentrations to below control levels in standing water samples. Both tested doses of ZOP (0.37 and 1.0 mg/L as Zn) resulted in reduction of lead and copper; however, the higher dose had more significant reductions. In addition, the higher dose lowered lead levels earlier in the term of the study than did the lower dose. The test loop (Loop 7), which had the higher ZOP dose and the higher pH, had problems with spiking of copper and zinc.

The different standing times did not affect metal levels in the pH–alkalinity loops. However, the length of standing time did have some influence on the effectiveness of ZOP. The higher dose ZOP loop experienced higher average copper and zinc levels with a longer standing time; however, lead levels in Loop 7 were similar at both standing times.

Acknowledgements

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