

CHAPTER 5

Effect of Phosphate Inhibitors on Lead Release From Pipes

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KEYWORDS: lead, phosphate inhibitors, corrosion by-products, potable water

ABSTRACT

Hexametaphosphate tends to increase release of both particulate and soluble lead to drinking water. For every mg/L of residual hexametaphosphate, soluble lead increased by 1.6 – 2.5 mg/L after 72 hour stagnation in pure lead pipes compared to the same condition dosed with orthophosphate. Utilities should consider these adverse effects whenever polyphosphate is used to prevent scaling or iron precipitation; in fact, polyphosphates cannot be recommended for lead corrosion control. Though soluble lead release was in reasonable agreement with predictions of solubility models, particulate lead release was dominant in these experiments. In some cases, a peak in lead release was observed with increasing stagnation time in pipes—analysis of that data indicated that particulate lead can re-attach to the pipe surface under at least some circumstances.

INTRODUCTION

The beneficial use of phosphates in preventing calcium scale build-up and iron precipitation in water distribution systems has been established for well over 50 years.¹ It is also known that, under at least some circumstances, phosphates can also prevent certain aspects of iron pipe corrosion including red water, weight loss and tubercle build-up.^{1,2,3} Consequently, when the USEPA Lead and Copper Rule effectively expanded the meaning of the term “corrosion control” at utilities to explicitly consider lead and copper concentrations at the consumers tap, it was hoped that phosphate dosing would provide a low cost approach to meeting multiple water quality objectives.⁴

Phosphates can be dosed as either phosphoric acid, combinations of orthophosphoric acid and zinc orthophosphate, polyphosphates, or blends of orthophosphoric acid and polyphosphate. More than one half of U.S. utilities reported that control of lead corrosion by-products was an important reason why they used phosphate based corrosion inhibitors in a 1992 survey.^{5,6} A

follow-up survey in 1994 suggested that usage had increased markedly as water utilities gradually complied with provisions of the United States Environmental Protection Agency (USEPA) Lead and Copper Rule.⁷ About one-third of utilities dosing phosphate inhibitors used either orthophosphate or zinc orthophosphate, while the remainder dosed either pure polyphosphate or a blend of polyphosphate and orthophosphate.

The type of phosphate dosed is important because simplistic solubility models (Figure 5-1) predict that orthophosphates and polyphosphates might have opposing effects.^{8,9} That is, dosing of orthophosphate might be predicted to decrease lead solubility through formation of relatively insoluble scales. In contrast, dosing of polyphosphate inhibitors might be expected to increase lead solubility—previous research clearly established the strength of the lead polyphosphate complex and the probability it would increase lead leaching to potable water.^{8,9} To the extent that soluble metals are the cause for higher lead and copper at the consumers tap then, dosing of polyphosphates could be increasing consumer exposure to lead and copper in drinking water. While this hypothesis is controversial and has been debated for at least a decade,^{10,11} recent monitoring data suggests that there is at least some merit to the concerns,^{5,12} even though the experimental designs did not always support drawing of explicit cause and effect relationships.

Previous research into effects of polyphosphates is unavoidably complicated by many factors, not the least of which is reversion of polyphosphates to orthophosphates in water distribution systems.¹³ That is, water sampled at consumers homes will invariably contain significant concentrations of orthophosphate, even if only polyphosphate is dosed at the treatment plant.^{14,15} Obviously, under such circumstances it is impossible to exclusively attribute possible benefits or detriments exclusively to orthophosphate or polyphosphate, since the net effect involves an interaction between the two.

This work is designed to provide some unambiguous answers as to phosphate effectiveness in controlling soluble lead release in representative tap waters. Pipe age is a key consideration in this analysis, and a unique approach was employed to determine relative effects of inhibitors in pipes after a few weeks, a few months and a few years of aging. An attempt was also made to sort out the relative impact of polyphosphates versus orthophosphates.

EXPERIMENTAL METHODS

Pipe rig tests were conducted to illustrate changes in lead corrosion by-product release in response to water quality changes and aging.¹⁶ The rigs were 12" long, 3/4" diameter pure lead pipes with a volume of approximately 100 mL. Number two rubber stoppers were used to plug the ends of each tube. All pipes were initially rinsed three times with 0.1 N sodium hydroxide (NaOH) and then rinsed five times with reagent grade (Milli-Q) water. Boulder, CO tap water (Table 5-1) was used as a base water, with appropriate modifications using carbon dioxide gas, perchloric acid or NaOH to achieve other targeted pH and alkalinity conditions (Table 5-2). These pH and alkalinity conditions were identified by Dodrill to be of "highest interest" with respect to phosphate inhibitor use in a national utility survey.⁶

For each of the above water qualities, three phosphate conditions were tested (no inhibitor, orthophosphate, and hexametaphosphate), making 15 water conditions total (5 water qualities x 3 inhibitor conditions). This allows direct and unambiguous comparison of inhibitor effects in a given water.

Stock solutions of orthophosphate and polyphosphate inhibitors were prepared at concentrations of 500 mg/L and 320 mg/L as P, respectively, and were kept in the dark at 4°C. For experiments with inhibitors, phosphates were dosed at a concentration of 1.0 ± 0.05 mg/L. The background concentration of phosphate in Boulder tap water was < 0.03 mg/L.

To test the effects of aging on lead corrosion by-product release, one batch of pipes was exposed to water beginning in June 1994, while other batches were exposed beginning in January 1997 and June 1997. During the 72-hour sampling event described in this work, these pipes had experienced 3 years, 6 months and 2 weeks of exposure, and are termed "old," "new" and "brand new" in subsequent discussion, respectively. These pipes were two weeks older during the 8-hour sampling event described later in this work. In total, therefore, 45 lead pipes were tested in these experiments (3 pipe ages x 3 inhibitor conditions x 5 water qualities). Unfortunately, though the lead pipe used in the "brand new" experiments was made by the same manufacturer, it was not produced in the exact same batch and was 50% larger diameter than that produced for the new and old tests. This factor was considered in subsequent analysis.

The pipes were maintained by regular water changes each Monday, Wednesday, and Friday for the duration of the study. To change the water, a pipe was first inverted three times to mix the water, then all of the water was poured out. The pipe was immediately refilled with fresh solution of the appropriate water quality. The pipes were laid flat and water inside the pipes was stagnant in between water changes.

On occasion, the pipes were intensively sampled to determine characteristics of lead by-product release to the water. Replicate samples were collected from the pipes for three successive stagnation periods (e.g. Sunday, Wednesday, and Saturday for the 72-hour experiment) so that the mean, standard deviation, and 95th percentile confidence interval of release from each pipe could be calculated. While this protocol has some obvious limitations in comparison to actual exposure in distribution systems in terms of stagnation time, pressures and shear forces, the advantage over other more complicated flow through apparatus is absolute control over water quality—the key focus of this work.

Lead and total phosphorus were analyzed by an inductively coupled plasma emission spectrophotometer (ICP-ES) according to Standard Method 3500 or 4500, respectively.¹⁷ Total lead was determined after acidifying samples with 1% nitric acid, whereas soluble lead was operationally defined using filtration through a 0.45- μm pore size syringe filter. Since colloidal species that can sometimes pass through this filter, the filtration approach represents an upper bound to truly soluble lead. Orthophosphate was distinguished from polyphosphate using a colorimetric test with ascorbic acid as described in Standard Method 4500-P.E.¹⁷ Quality assurance and quality control established that lead or phosphorus species were not sorbing to filters or sample bottles.

RESULTS AND DISCUSSION

Two approaches were used in this work to gain insight into effects of time on by-product release phenomena. First, by-product release was tracked from a single pipe for a time period as long as 4 years. Second, because a real tap water was used for the study, with inherent typical seasonal and other variations in water quality, another experiment was conducted in parallel in which pipes were exposed for a few months or a few weeks. By measuring by-product release from all these pipes on the same day using the same water, effects of aging can be determined

directly. At various points in the sampling, particulate and soluble metals were determined, along with measurement of phosphate residuals and speciation.

At the outset, we note the potential limitations of the work. First, there is no guarantee that trends noted in this study for inhibitors will be directly transferable to other waters of similar pH and alkalinity. While it is believed that pH and alkalinity are two of the most important factors influencing corrosion and inhibitor behavior, other factors such as chloride, hardness, disinfectant type and dose, stagnation and flow, temperature, and other factors are undoubtedly important under at least some circumstances. Secondly, with respect to lead release, it is well known that mechanisms of release differ based on the source of lead (i.e., brass, pure lead, lead-tin solder, etc), whether the material is galvanically coupled to a more noble metal such as copper, and other factors. This work exclusively examined the effects of water quality on corrosion of pure lead pipes. Given the lack of information regarding corrosion of other lead-containing plumbing materials, it is often assumed that trends noted for pure lead apply. While this assumption provides some basis for decision-making, we note that the validity of this hypothesis has not been rigorously tested, and in fact there is reason to believe that it is not valid in many circumstances. Thus, as with any research, the results described below must be applied cautiously to other situations.

Effects of Aging, Inhibitors and Stagnation Time on Total Lead Release

One perspective on the role of aging and water quality in lead by-product release can be obtained by tracking a single pipe over a long time period of consistent exposure. Since all experimental solutions started with “real” tap water, factors impacting release from these pipes include aging, seasonal effects, and subtle changes in water quality parameters other than pH and alkalinity such as TOC, sulfate, chloride and other ions.

For lead pipes without inhibitors at pH 7.2, by-product release was much lower at 45 and 300 mg/L alkalinity than at 15 mg/L alkalinity (Figure 5-2) in new pipes. The benefits of higher alkalinity at this pH are nearly all accrued in the change from 15 to 45 mg/L. With aging, by-product release dropped by about an order of magnitude at pH 7.2 at 4 months versus 3 years at alkalinity of 15 mg/L as CaCO₃; however, at the higher alkalinity aging did not appear to decrease by-product release that much over the same timespan. Nevertheless, benefits of

alkalinity 45 mg/L versus 15 mg/L alkalinity were still very substantial. Examining pipes at constant dissolved inorganic carbon (DIC) and varying pH (Figure 5-3), lead release in the absence of inhibitors is also benefited by higher pH. The effect tends to be relatively linear with pH regardless of pipe age, in contrast to the apparent threshold effect of alkalinity. Lead release lessened as the pipe aged from 4 months to 3 years, with more significant percentage improvements from aging at the higher pH.

The benefits of inhibitors are noteworthy even on a logarithmic scale at pH 7.2 and 15 or 45 mg/L as CaCO₃ at most time periods. The most obvious exception to this is at pH 7.2, alkalinity 300 mg/L, for which polyphosphate clearly increased lead release compared to the system with orthophosphate or no inhibitor in relatively new pipes. As a general rule, by-product release decreased about 0.5–1 order of magnitude with aging over the 3 year experiment, although a much more substantial improvement was noted for pipes at pH 7.2, alkalinity 15 mg/L as CaCO₃. Consistent with predictions based on solubility models and utility monitoring data, the lowest lead releases were noted at pH 9.5 with or without inhibitor dosing,^{7,18-20} although very low levels of release were also obtained at pH 7.2, 300 mg/L as CaCO₃ without inhibitor.

For another perspective on aging, it is interesting to determine whether or not these trends can be confirmed with statistical confidence for the pipes aged different time periods, but exposed to the exact same water on the same day. In pipes without inhibitors, the trend of lower lead release with higher alkalinity at pH 7.2 was confirmed at greater than 95% confidence for all pipe ages (Figure 5-4). This was also the case when the test was repeated with an 8-hour stagnation, except that a high variability in lead release at pH 7.2, alkalinity 15 mg/L for the 3 year old pipe decreased the significance of the trend to less than 95% confidence (Figure 5-5). Generally, lead release significantly decreased with aging, although an unusual worsening of release was noted in pipes aged 6 months at pH 7.2 and 7.8 without inhibitors when compared to the same condition at 2 weeks age. This might be at least partly attributable to the 50% larger diameter of the pipes aged just two weeks as noted earlier, an interpretation consistent with the fact that increased lead release was not observed during this time period for data in Figure 5-2.

The relative benefits of inhibitors can be assessed by the following equation:

$$\% \text{ Change} = \frac{(\text{Pb release with inhibitor} - \text{Pb release without inhibitor})}{\text{Pb release without inhibitor}} \times 100\% \quad (5-1)$$

In this calculation, benefits due to inhibitor dosing results in negative numbers whereas detrimental effects result in positive numbers. In the discussion that follows, only “significant” effects of greater than 95% confidence are presented, although trends of lesser confidence are clearly apparent in Figure 5-4 and 5-5. A broad compilation of inhibitor effects for the two stagnation times, differing pipe ages and all water qualities is instructive (Figure 5-6). Orthophosphate dosing often led to > 70% decreases in lead release. This was true for both the 8- and 72-hour stagnation times at every water quality tested at 6 months pipe age. In pipes aged 3 years, orthophosphate significantly (greater than 95% confidence) reduced lead release for all conditions except pH 7.2, alkalinity 15 mg/L. The only detrimental impacts from dosing orthophosphate were in new pipes (aged 2 weeks) with a 72-hour stagnation time in waters at pH 7.2, alkalinity 300 mg/L and pH 7.8, alkalinity 45 mg/L.

In contrast, effects of hexametaphosphate dosing were more frequently detrimental than beneficial when compared to the same condition without inhibitor. In fact, during the 8-hour stagnation sampling the only benefit was at pH 7.2, 15 mg/L alkalinity at 6 months pipe age. In the very new (2 weeks) and the oldest pipes (3 years), hexametaphosphate was highly detrimental to lead release at pH 7.2, alkalinity 300 mg/L for both an 8- and 72-hour stagnation time, with as much as a 591% increase in lead release. This confirms trends noted earlier in this water when tracking release from a given pipe over a 3 year timespan (Figure 5-2). In contrast, pH 7.2, alkalinity 300 mg/L as CaCO₃ was the only condition for which adverse effects from hexametaphosphate were still significant at greater than 95% confidence after 3 years.

One of these results was particularly perplexing and deemed worthy of follow up study. For the condition at pH 7.8, alkalinity 45 mg/L, polyphosphate significantly worsened lead release for the 2 week old samples and improved release in the older samples for a 72-hour stagnation time. In contrast, polyphosphate had nearly no effect at 8-hour stagnation regardless of pipe age. To attempt and better understand how these results could possibly occur, the pipes were re-sampled at stagnation times of 3, 5, 8, 24, and 72 hours. This was not a triplicate analysis and we further note that the pipe that had been aged 2 weeks was now 4.5 months old by

the time this experiment was conducted. Nevertheless, as noted before in the triplicate analysis, by-product release followed some unusual trends with time in these pipes (Figure 5-7).

For the most part, soluble lead increased with time before leveling off after about 3 hours. In the older pipe samples, total lead release followed the same pattern, although lead release in samples with hexametaphosphate leveled off at much lower values than in the sample without hexametaphosphate. In the newer samples, total lead release appeared to peak after about 5 hours, after which time it dropped sharply before eventually leveling off. This caused the perplexing result that, after 72-hours stagnation for the new samples, the system with hexametaphosphate had higher lead whereas the opposite was true for time periods less than 24 hours.

The above result is interesting because this type of release, with a peak at 5 hours followed by a decrease thereafter, has been reported previously for copper under anoxic conditions.²¹ The other noteworthy finding is that the initial peak in release clearly arose from mostly particulate lead, which seemingly “re-attached” to the pipe wall, while in the past re-attachment has been attributed to soluble metal redox changes.^{21,22} Finally, this unusual release curve reinforces the limitations of this work; conclusions based on the 8-hour and 72-hour sampling events, which provide important snapshots of by-product release trends in time, cannot always be extrapolated with confidence to other stagnation times.

Changes in Soluble Phosphorus During Stagnation

The previous sections described trends in total lead release, which represents the combined result of particulate and soluble lead. This section takes a closer look at chemical changes taking place in pipes during stagnation events, as well as factors influencing the concentration of soluble lead after stagnation. Changes in particulate lead are discussed in detail elsewhere.¹⁵ The chemical changes deemed most important for tracking included pH, phosphate consumption and polyphosphate reversion to orthophosphate. During stagnation, pH tended to increase markedly in the pipes, although the magnitude of the shift tended to decrease with pipe age (Figure 5-8). There were no clear trends between pH after stagnation and either soluble or total lead release; however, it is interesting to note that the final pH was higher in the pipes without inhibitors in most cases. This might be part of the reason why benefits of

orthophosphate may have taken longer aging times to achieve in these experiments; higher pH generally reduced lead release, and in newer pipes final pH was often higher in waters without inhibitors.

During the 8-hour stagnation event, there was always some soluble phosphate remaining in the water, although as much as 90% of the phosphate was consumed in some cases (Figure 5-9). Consumption of orthophosphate was inversely related to alkalinity. That is, nearly no phosphate was consumed in the high alkalinity water at pH 7.2 after 8 hours stagnation, whereas the highest consumption was noted for the lowest alkalinity water at the same pH. This would be expected if a lead carbonate solid was forming preferentially to a lead phosphate solid at higher alkalinity, or if there was a higher rate of lead corrosion at higher alkalinity.

In 12 of 15 cases, significantly less hexametaphosphate was consumed than orthophosphate. This was most extreme at pH 7.8, alkalinity 45 mg/L in new pipes, for which no hexametaphosphate was consumed and nearly 85% of the orthophosphate was consumed on some occasions. Tests also demonstrated that a substantial portion of the hexametaphosphate was reverting to orthophosphate during the 72-hour stagnation event, and the extent of reversion tended to increase with pipe age.¹⁵ At pH 7.2, alkalinity 45, as much as 80% of the residual soluble phosphate had been converted to ortho-P during 72-hour stagnation, and at least 20% of the soluble phosphorus was present as orthophosphate at the other conditions. Thus, the polyphosphates are more readily converted to orthophosphates in older pipes, with concomitant advantages to lead release as will be discussed later.

A Closer Look at Soluble Lead Release During Stagnation

Soluble lead concentrations in the pipes were always lower in the presence of orthophosphate than in an equivalent system without inhibitor (Figure 5-10). One of the most interesting observations is that, in the absence of inhibitors, soluble lead concentrations did not change much with time. Even with inhibitors, where effects of aging on solubility were more significant, decreases in solubility were typically only about 50% (comparing the brand new and oldest pipes). This is in marked contrast to copper pipes, where solubility is a very strong function of pipe age in some circumstances.

The actual levels of soluble lead agree reasonably well to that predicted by cerussite solubility (Figure 5-11 versus Figure 5-10) in the absence of inhibitors. The exception is the data at pH 9.5, which is more consistent with the lower solubility hydrocerussite as would be expected based on solubility models (i.e., Figure 5-11 and discussion in Schock et al., 1983²⁰). Likewise, levels of soluble lead in the presence of orthophosphate are in the range of 0.02 to 0.3 mg/L, which is expected based on the levels of 0.1 mg/L predicted in the presence of 1 mg/L as P residual (Figure 5-10 versus 5-11). Note that the actual levels of residual phosphate were less than 1 mg/L in pipes due to consumption of inhibitor as will be discussed later, and this likely accounts for the levels of lead higher than 0.1 mg/L observed in the pipes. In addition, particulate lead was so high in these samples that it is quite likely that a substantial portion of the lead that was defined as “soluble” in Figure 5-9 was actually colloidal. In any case, soluble lead levels are neither unusually high or low in comparison to expectations outlined in Schock^{9,18-20}

In every instance soluble lead concentrations were lower in the presence of orthophosphate than in an equivalent system without inhibitor (Figure 5-10). Conversely, with very few exceptions, soluble lead concentrations were higher in systems dosed with hexametaphosphate than without inhibitor. Therefore, in terms of relative performance of the two inhibitors in controlling soluble lead release, orthophosphate has an enormous advantage. To highlight this effect, the percentage increase in soluble lead due to hexametaphosphate dosing compared to orthophosphate can be calculated as:

$$\% \text{ Increase} = \frac{(\text{Pb release with hexameta-P} - \text{Pb release with ortho-P})}{\text{Pb Release with ortho-P}} \times 100\% \quad (5-2)$$

This demonstrates that hexametaphosphate increased lead release in every instance when compared to an equivalent dose of orthophosphate (Figure 5-12). The minimum increase was 100%, or a doubling of the soluble lead concentration. The most pronounced effect was at pH 7.2, alkalinity 45 mg/L in pipes aged 3 years, for which hexametaphosphate increased soluble lead by 3500%. There can no longer be any doubt that hexametaphosphate substantially increases problems with soluble lead under a wide range of circumstances, effecting ending debate on this controversial subject.^{5,8,10,11,12} Moreover, the magnitude of the observed effects are very disturbing to say the least.

Extensive attempts were made to model the increase in soluble lead using a simplistic approach that proved successful previously for copper.¹⁵ The initial assumption is that polyphosphate complexes were exclusively responsible for the “excess” concentration of soluble lead observed in pipes dosed with hexametaphosphate versus orthophosphate. If so, a term “excess soluble Pb” is defined as:

$$\text{“Excess soluble Pb”} = \text{Soluble lead}_{\text{poly-P}} - \text{Soluble lead}_{\text{ortho-P}} \quad (5-3)$$

If the Pb-polyphosphate complex is very strong, then under some circumstances it can be shown that the following relation will hold:

$$\text{Excess Soluble Pb} = K [\text{Total Poly-P}] \quad (5-4)$$

where K is a constant.

There was a reasonable correlation between “excess soluble Pb” and residual polyphosphate over the entire range of pH and alkalinity conditions tested, with a “best fit” K value of 1.6 for all data points ($R^2 = 0.6$). In other words, every 1 mg/L of residual polyphosphate P had an average complexation capacity of 1.6 mg/L lead. This value is in reasonable agreement with the 2 mg/L of lead complexation capacity determined for this polyphosphate in laboratory experiments using competing ligand spectroscopy.¹⁵ Although the lab studies found that complexation capacity was relatively insensitive to pH,¹⁵ better correlation coefficients were obtained when the pipe data were sorted by initial pH (Figure 5-13). The K values obtained were 1.9 ($R^2 = 0.7$) for pH 7.2 and 7.8 waters, and 2.5 ($R^2 = 1.0$) for pH 9.5.

It should be noted that the lead complexation capacity would not be realized under many circumstances. For example, in waters with higher hardness than was present in this work (Table 5-1), a substantial fraction of the polyphosphate that might have complexed lead is complexed by hardness ions, thereby decreasing the maximum level of lead dissolution.^{9,15} Likewise, if pure lead pipes were not used, it is unlikely that the water would fully equilibrate with lead scale phases.⁹ However, realizing only 10% of the theoretical complexation would translate to an additional 20 µg/L lead if residual polyphosphate was 0.1 mg/L P. Thus, the effect could be quite serious whenever a drinking water with residual polyphosphate contacts brass, solder, or other lead bearing materials, considering the stringent lead action limit of 15 µg/L.

Recommendations to Utilities Either Dosing or Considering the Dosing of Polyphosphates

On the basis of these and other results,^{5,8,12} polyphosphate cannot be recommended for lead corrosion control without extensive testing providing proof to the contrary of this research. It is quite possible that under certain circumstances not tested in this study polyphosphate dosing could decrease lead release. For example, if extensive reversion to orthophosphate occurred before the water contacted lead bearing plumbing materials in consumers' homes, benefits from the produced orthophosphate could outweigh detriments from the remaining polyphosphates. Of course, given that very little is known about reversion kinetics in water distribution systems, it seems risky to rely on reversion reactions to produce the desired benefits.

It is important to reiterate that polyphosphate still has important benefits in prevention of scaling and precipitation of iron or manganese, and for certain types of iron corrosion control. Under circumstances where polyphosphate is dosed explicitly for these reasons, it would be worthwhile to determine the minimum polyphosphate dose that achieves these desired benefits, because detriments to maximum soluble lead in pipes during stagnation are expected to be proportional to residual polyphosphate (Figure 5-13). To ensure that less than 1 µg/L of soluble lead is complexed, however, would require residual polyphosphate of less than 0.0006 mg/L.

CONCLUSIONS

While orthophosphate dosing typically reduced soluble lead release by about 70%, there were exceptional cases in new pipes where increased lead was observed compared to the same system without inhibitor. One possible reason for adverse effects of orthophosphate, especially in new pipes, is that pH increased to a lesser extent during stagnation compared to the same condition without inhibitor.

Hexametaphosphate generally increased soluble lead release over a broad range of water qualities. Each mg/L of residual hexametaphosphate increased soluble lead release by about 1.6 mg/L compared to the same system with orthophosphate.

Soluble lead release was in reasonable agreement with predictions of solubility models. Soluble lead levels did decrease significantly with aging, but to a much lesser extent than particulate lead levels.

Particulate lead release was the dominant component of the total lead release in this work. In some cases, a peak in lead release was observed during stagnation. Analysis of the data suggested that particulate lead could re-attach to the pipe surface during long stagnation times.

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REFERENCES

1. Rice, O. and Hatch, G.B. Threshold Treatment of Municipal Water Supplies; Use of Sodium Hexametaphosphate. *Journal AWWA*, 31:7:1171-1185 (1939).
2. Vik, E.A., R.A. Ryder, I. Wagner and J. Ferguson. Mitigation of Corrosion Effects. In *Internal Corrosion of Water Distribution Systems, 2nd Edition*. AWWA Research Foundation and DVWG Technologiezentrum Wasser Denver, CO (1996).
3. McNeill, L.S. and Edwards, M. Phosphate Inhibitors and Red Water in Stagnant Iron Pipes. *Journal of Environmental Engineering*, in press (2000).
4. Boffardi, B.P. Potable Water Treatment and Monitoring For Corrosion and Scale Control. *Journal NEWWA*, 102:6:111-116 (1988).
5. Dodrill, D. and Edwards, M. Corrosion Control on the Basis of Utility Experience. *Journal AWWA*, 87:7:74 (1995).
6. Dodrill, D. Lead and Copper Corrosion Control Based on Utility Experience. University of Colorado MS Thesis (1992).
7. Edwards, M., Jacobs, S., and Dodrill, D. Desktop Guidance for Mitigating Pb and Cu Corrosion By-Products. *Journal AWWA.*, 91:5:66-77 (1999).
8. Holm, T., and Schock, M. Potential Effects of Polyphosphates Products on Lead Solubility in Plumbing Systems. *Journal AWWA*, 83:7 (1991).
9. Schock, M. R. I. Wagner and Oliphant, R.J. Corrosion and Solubility of Lead in Drinking Water. In *Internal Corrosion of Water Distribution Systems 2nd Edition*. AWWA Research Foundation and DVWG Technologiezentrum Wasser, Denver, CO (1996).

10. Boffardi B.P. Polyphosphate Debate. *Journal AWWA.*, 83:12:10 (1991).
11. Holm, T., and Schock, M., Reply to B.P. Boffardi. *Journal AWWA.*, 83:12:10 (1991).
12. Cantor, A.F., D.D. Charroff, R.R. Vela, M.G. Oleinik, and Lynch, D.L. Use of Polyphosphate in Corrosion Control. *Journal AWWA.*, 92:2:95-102 (2000).
13. Zinder, B., J. Hertz, and H. R. Oswald. Kinetic Studies on the Hydrolysis of Sodium Triphosphate in Sterile Solution. *Wat. Res.*, 18:5:509-512 (1984).
14. Goldberg, M. Advanced copy of final AWWARF report on “Analytical Techniques to Identify Phosphate Inhibitors.” AWWA, Denver, CO (1995).
15. Edwards, M., L. S. McNeill, T.R. Holm and Lawrence, M.C. Role of Phosphate Inhibitors in Mitigating Lead and Copper Corrosion By-product Release. AWWARF Final Report. AWWA, Denver CO (2000).
16. Lind-Johansson, E. Dissertation. Chalmers University of Technology, Department of Sanitary Engineering. Goteborg, Sweden (1989).
17. APHA. *Standard Methods for the Examination of Water and Wastewater. 20th Edition*, United Book Press, Inc; Baltimore, Maryland (1998).
18. Schock, M. R. Response of Lead Solubility to Dissolved Carbonate in Drinking Water. *Jour. AWWA* 72:695-704 (1980).
19. Schock, M. R. Understanding Corrosion Control Strategies for Lead. *Journal AWWA* 81:88-100 (1989).
20. Schock, M.R. & Gardels, M.C. Plumbosolvency Reduction by High pH and Low-Carbonate Solubility Relationships. *Journal AWWA*, 75:2:87 (1983).
21. Werner, W., et al. Corrosion of Copper Pipes in Drinking Water Installations. Translation of: *gwf-Wasser/Abwasser*, 135:2:1 (1994).
22. Edwards, M., and Sprague, N.M. Role of NOM in Copper Corrosion By-Product Release, A Mechanistic Study. *Corrosion Science*, in press (2000).

Table 5-1. Typical Ionic Constituents in Base Water

Parameter	Value	Units
Ortho-phosphate	<0.05	mg/L
Iron	1.1	mg/L
Lead	< 0.003	mg/L
Copper	< 0.01	mg/L
Silica	5-8	mg/L
Calcium	21	mg/L
Magnesium	7.6	mg/L
Chloride	6	mg/L
Fluoride	1.1	mg/L
Specific Conductance	93	µmhos/cm
Sulfate	6	mg/L
Free Chlorine	0	mg/L
Total Organic Carbon	1.28	mg/L

Table 5-2: pH and Alkalinity Modifications to Boulder Water for Pipe Experiments

pH	Carbonate Alkalinity (mg/L as CaCO ₃)	Adjustment to tap water.	Reason for Interest
7.8	45	no major adjustment required	No or adverse impacts for both lead and copper when polyphosphate inhibitors were dosed.
7.2	300	add NaHCO ₃ , bubble with CO ₂	Utilities had a high likelihood of exceeding the copper action—need an understanding of resultant inhibitor effects on lead release.
9.5	45*	add NaOH	Highly variable inhibitor impacts on lead release.
7.2	15	add HClO ₄ , bubble with air	Utilities with this approximate water quality have the highest likelihood of exceeding the EPA lead or copper action limit. All phosphate inhibitors effectively mitigated lead and copper corrosion by-products.
7.2	45	bubble with CO ₂	Phosphate inhibitors had beneficial effects for copper but had no or adverse impacts on lead corrosion by-products.

*60 mg/L total alkalinity

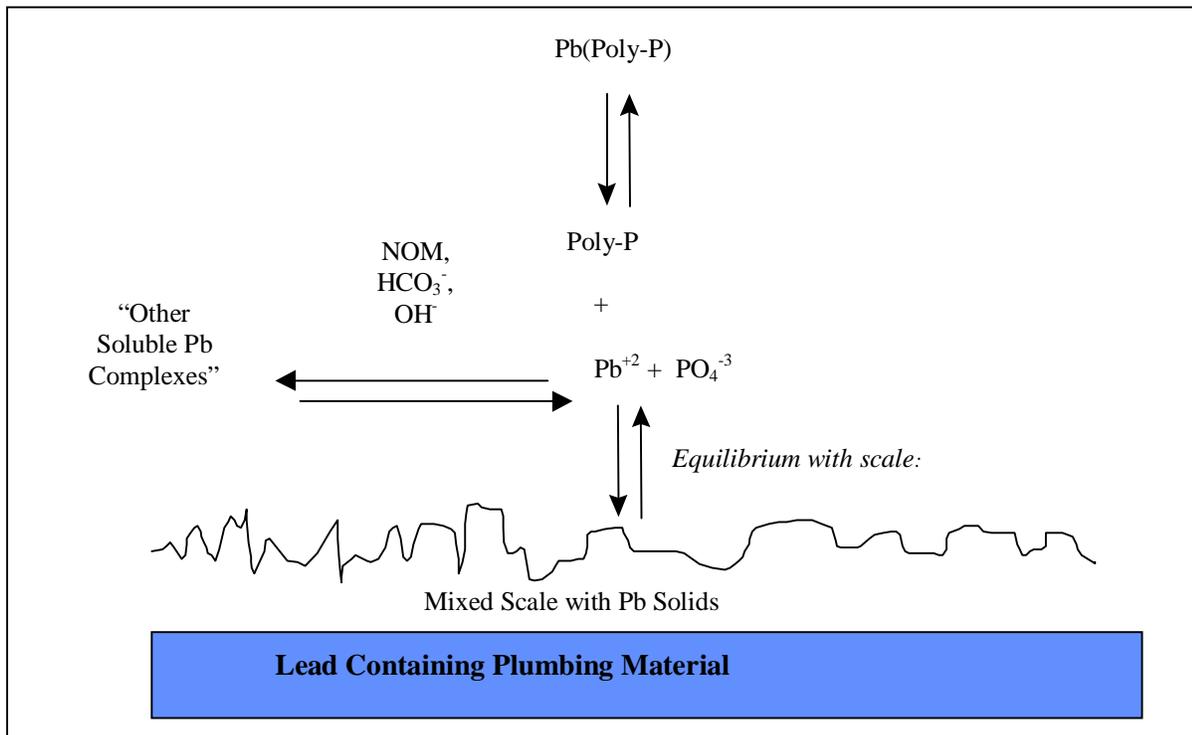


Figure 5-1. Simplistic conceptualization of factors influencing soluble lead concentrations at equilibrium after stagnation in waters dosed with hexametaphosphate and orthophosphate.

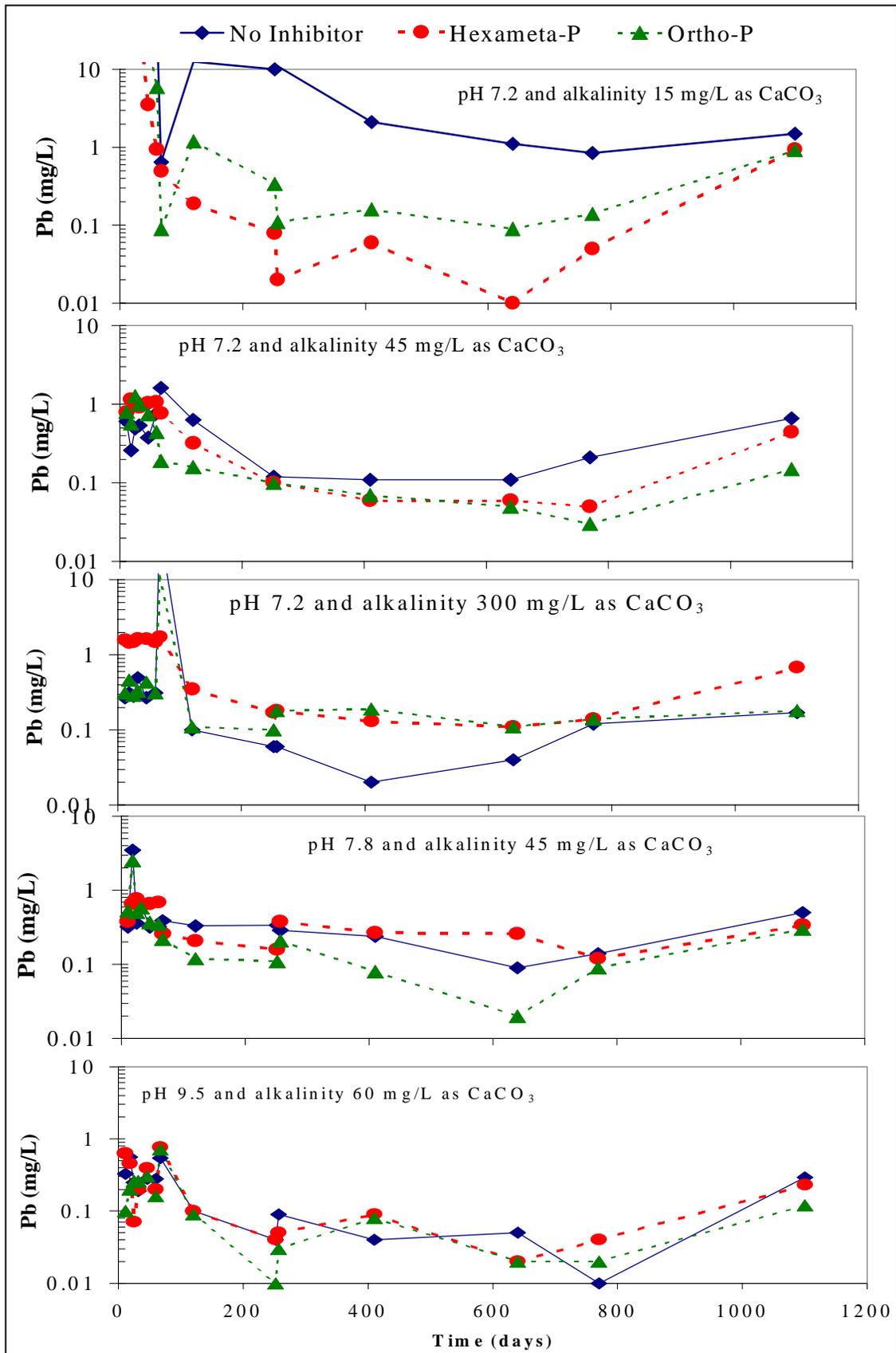


Figure 5-2. Total lead release from pipes after 72-hour stagnation.

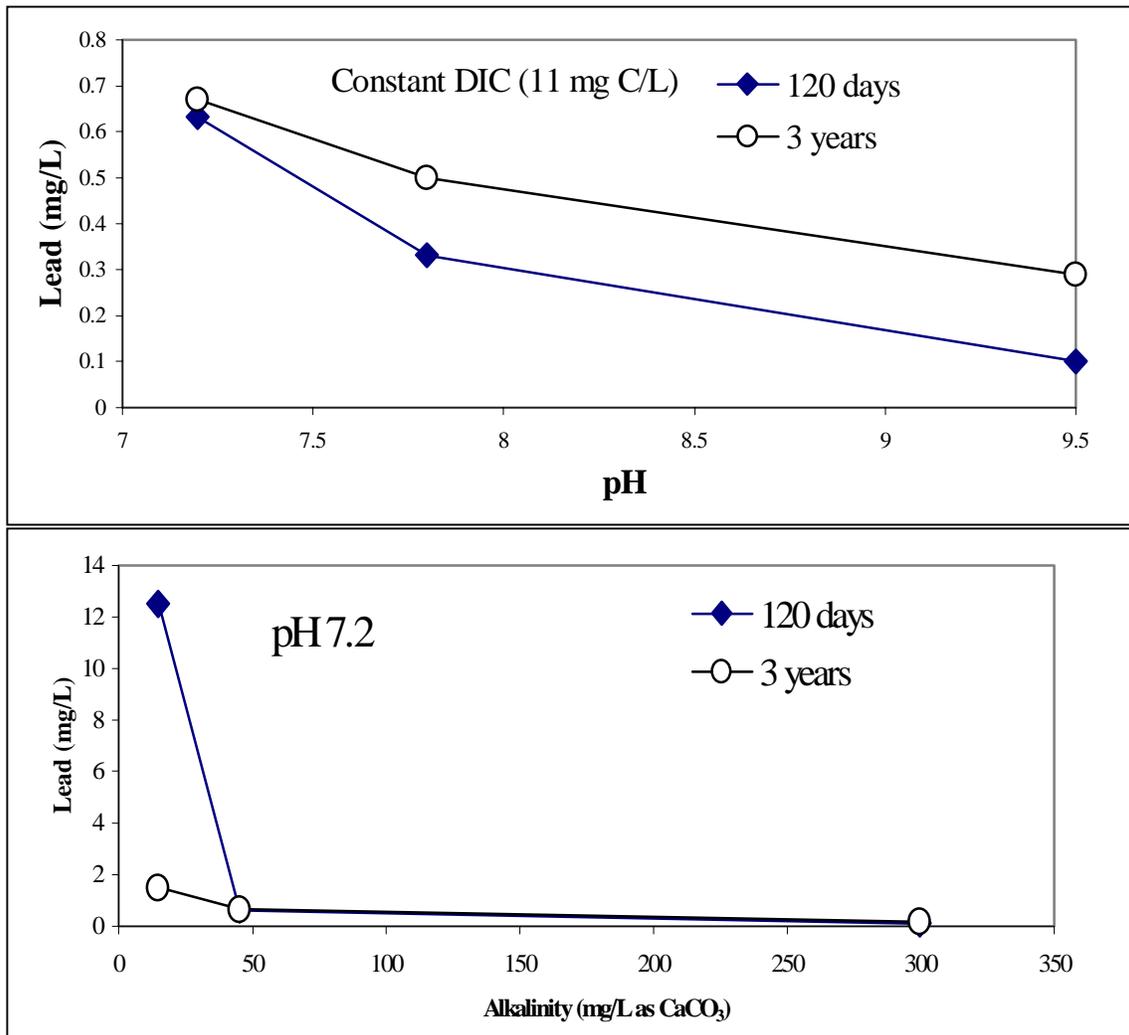


Figure 5-3. Effects of aging on lead release at constant DIC (upper graph) or constant pH (lower graph).

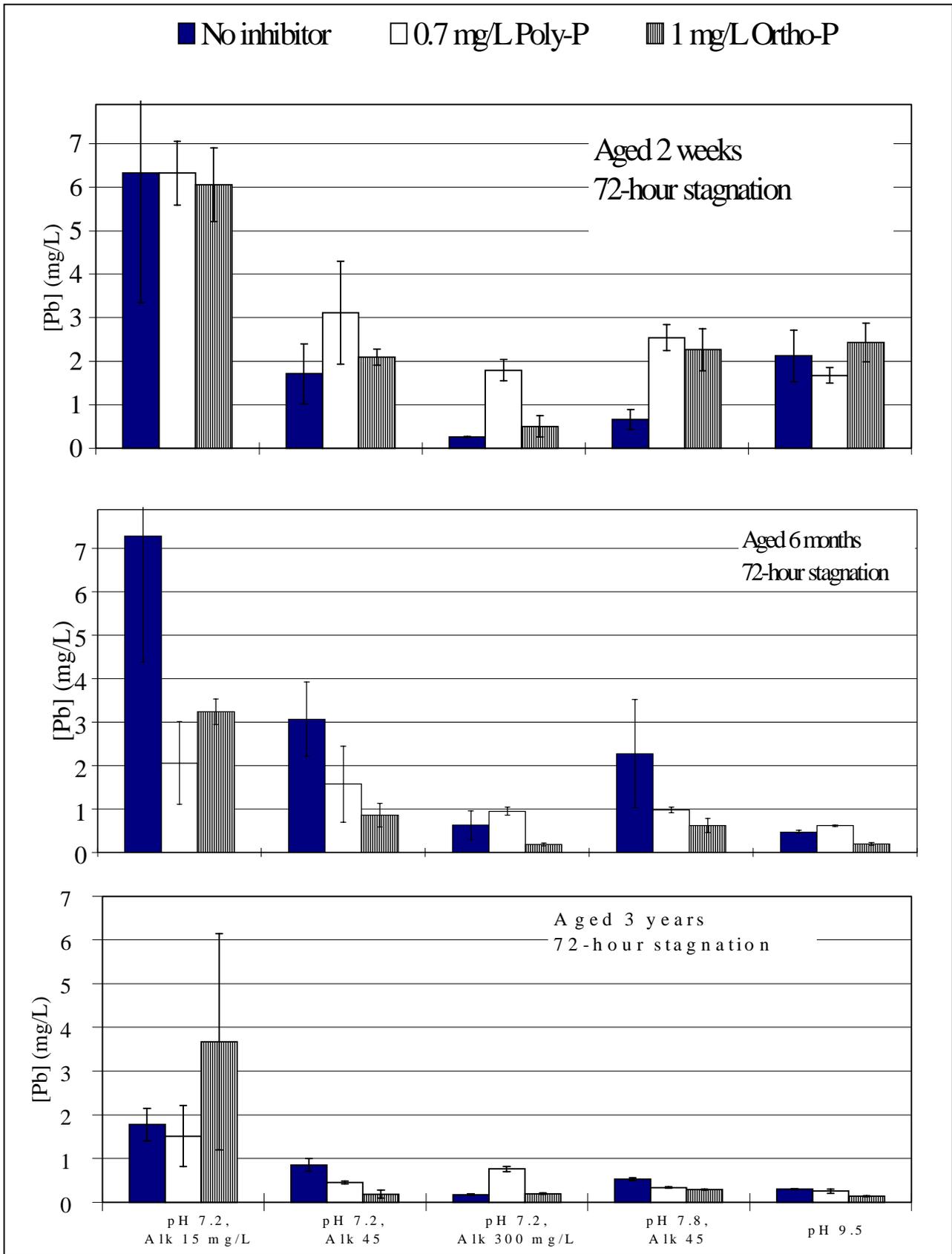


Figure 5-4. Total lead release during 72-hour sampling event. Error bars indicate 95% confidence interval based on triplicate samples.

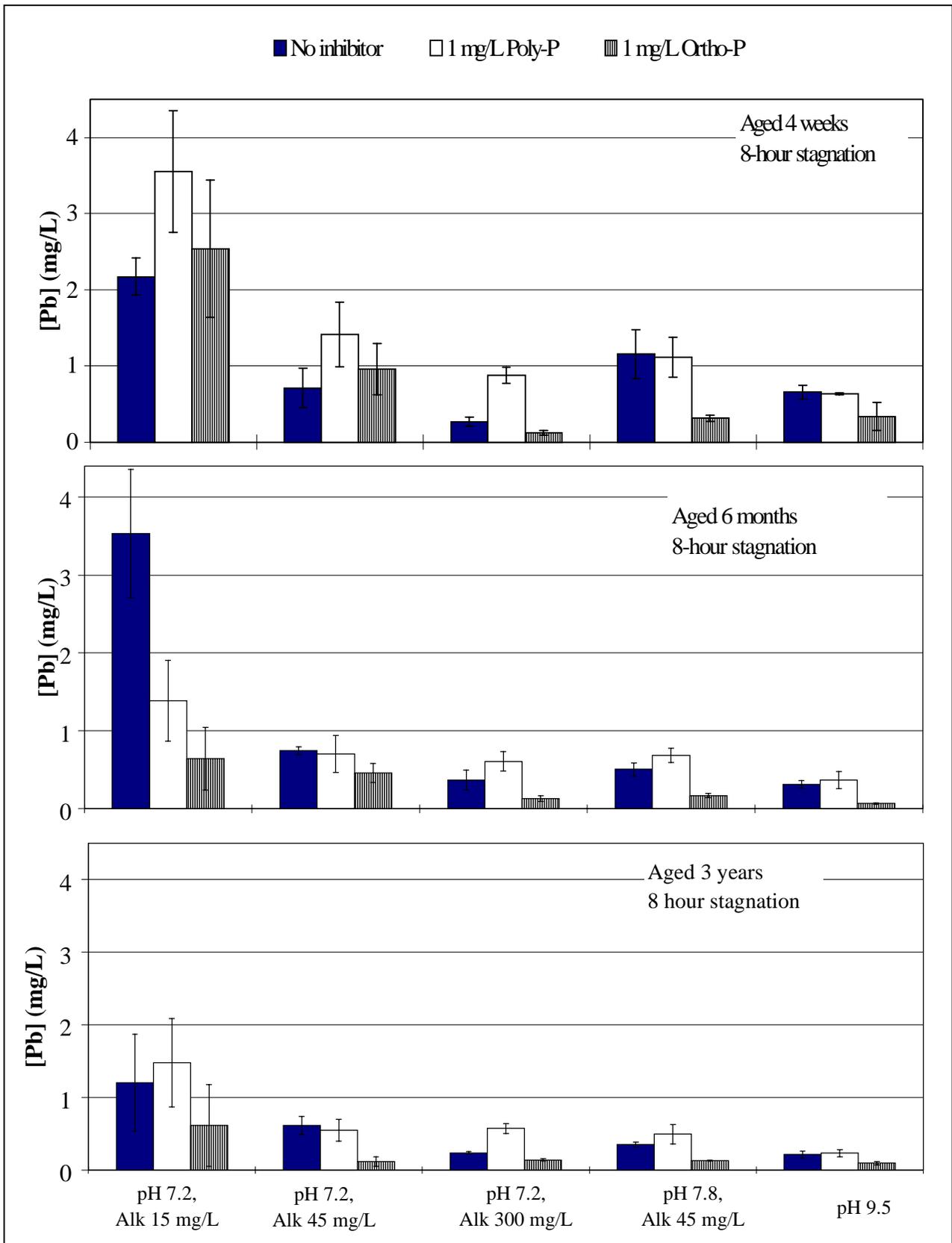


Figure 5-5. Total lead released during 8-hour sampling event. Error bars indicate 95% confidence interval based on triplicate samples.

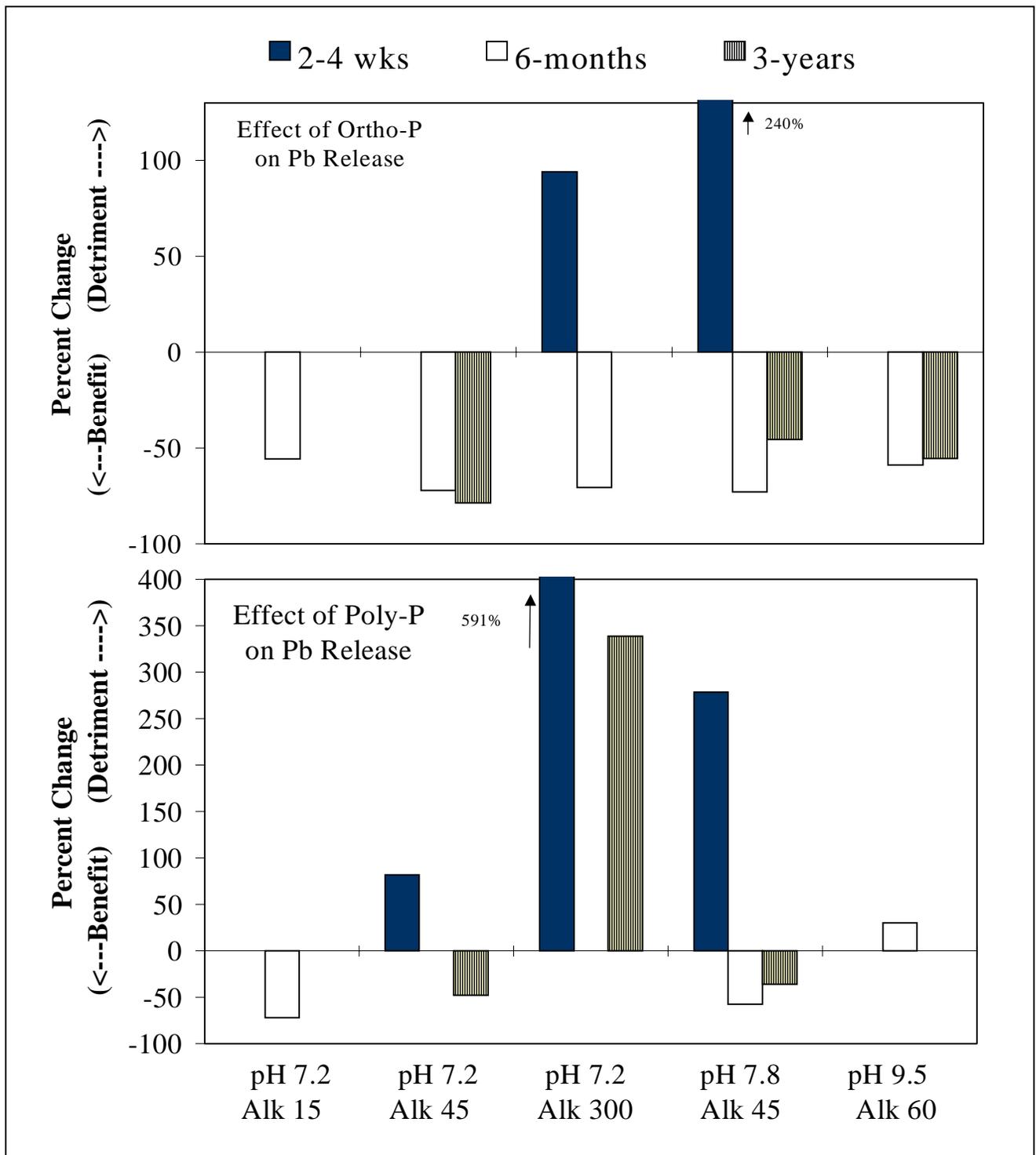


Figure 5-6. Relative impact of indicated inhibitor on total lead release for 72-hour triplicate sampling. Missing bars were not significant at 95% confidence when compared to the same system without inhibitor.

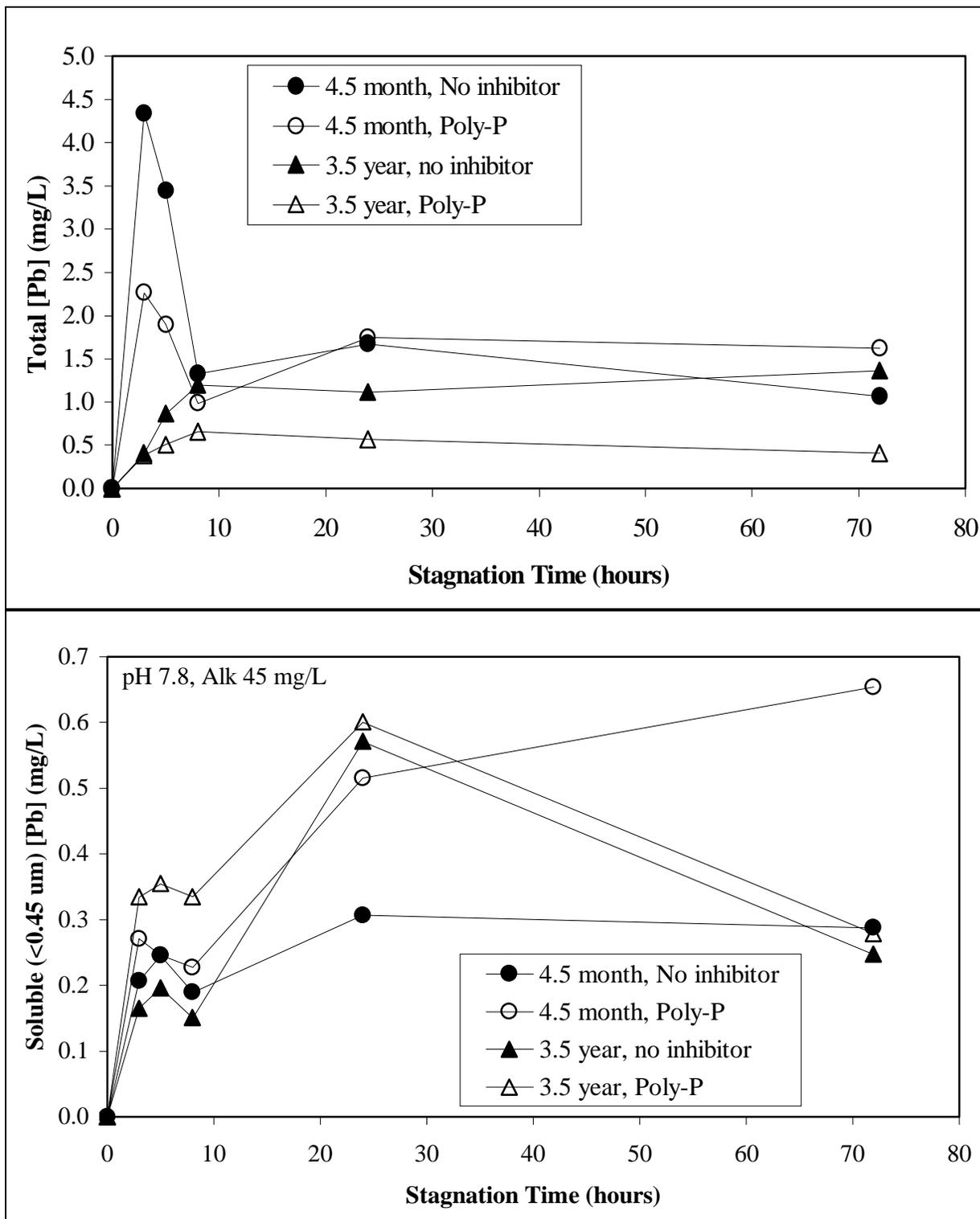


Figure 5-7: Lead release with time for old (aged 3.5 years) and brand new (aged 4.5 months) lead pipes at pH 7.8, alkalinity 45 mg/L.

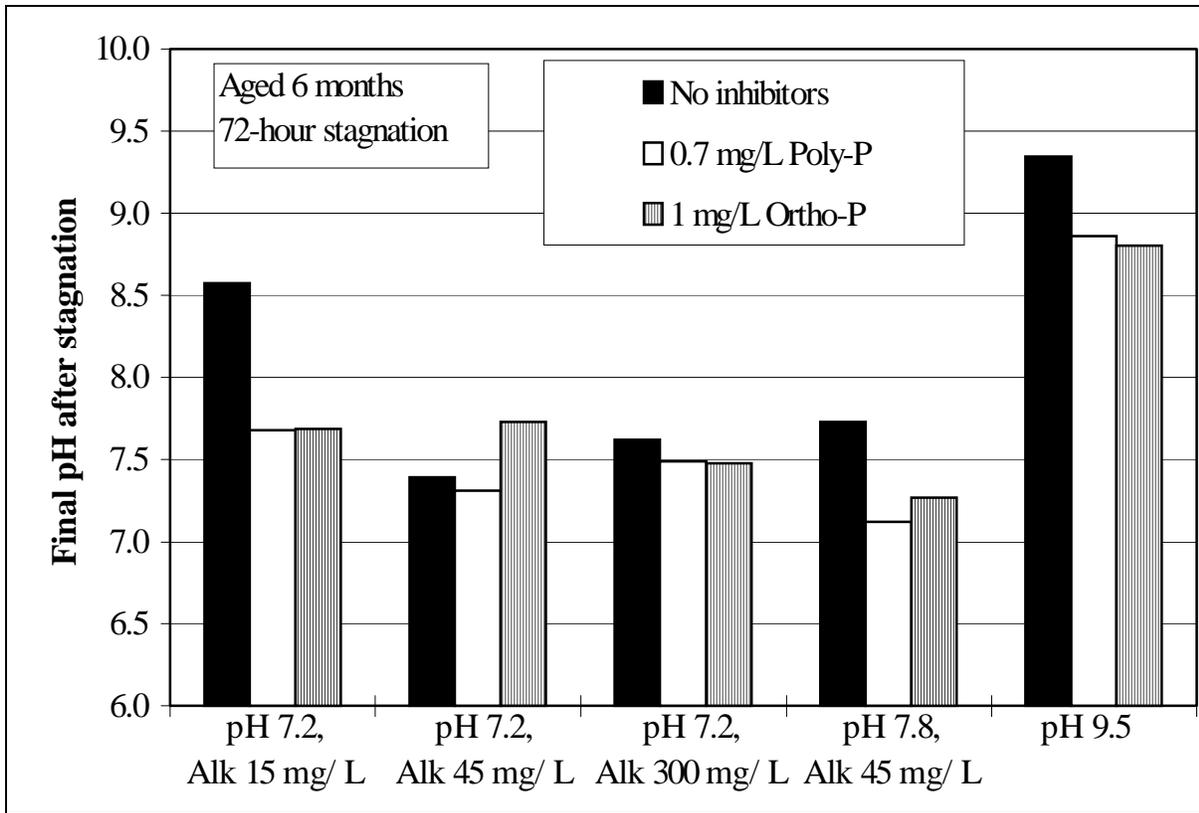


Figure 5-8. Final pH after 72-hour stagnation for new (aged 6 months) pipes.

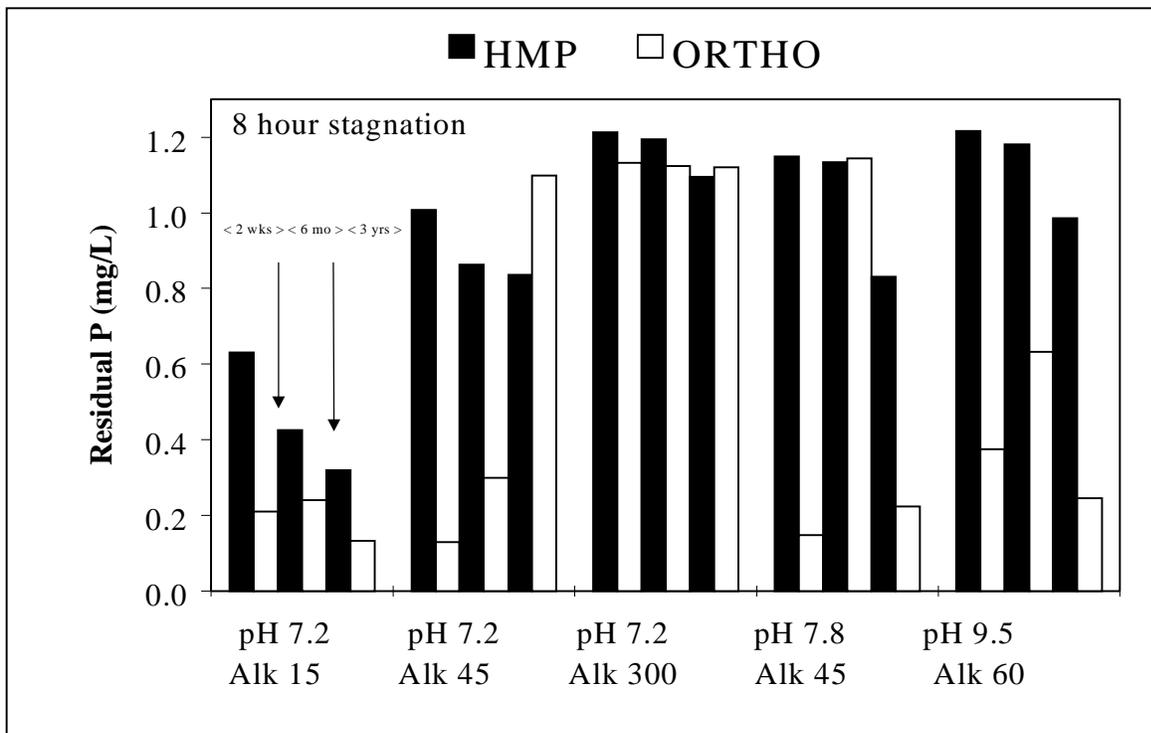


Figure 5-9. Phosphate residuals in pipes dosed with hexametaphosphate (HMP) and orthophosphate.

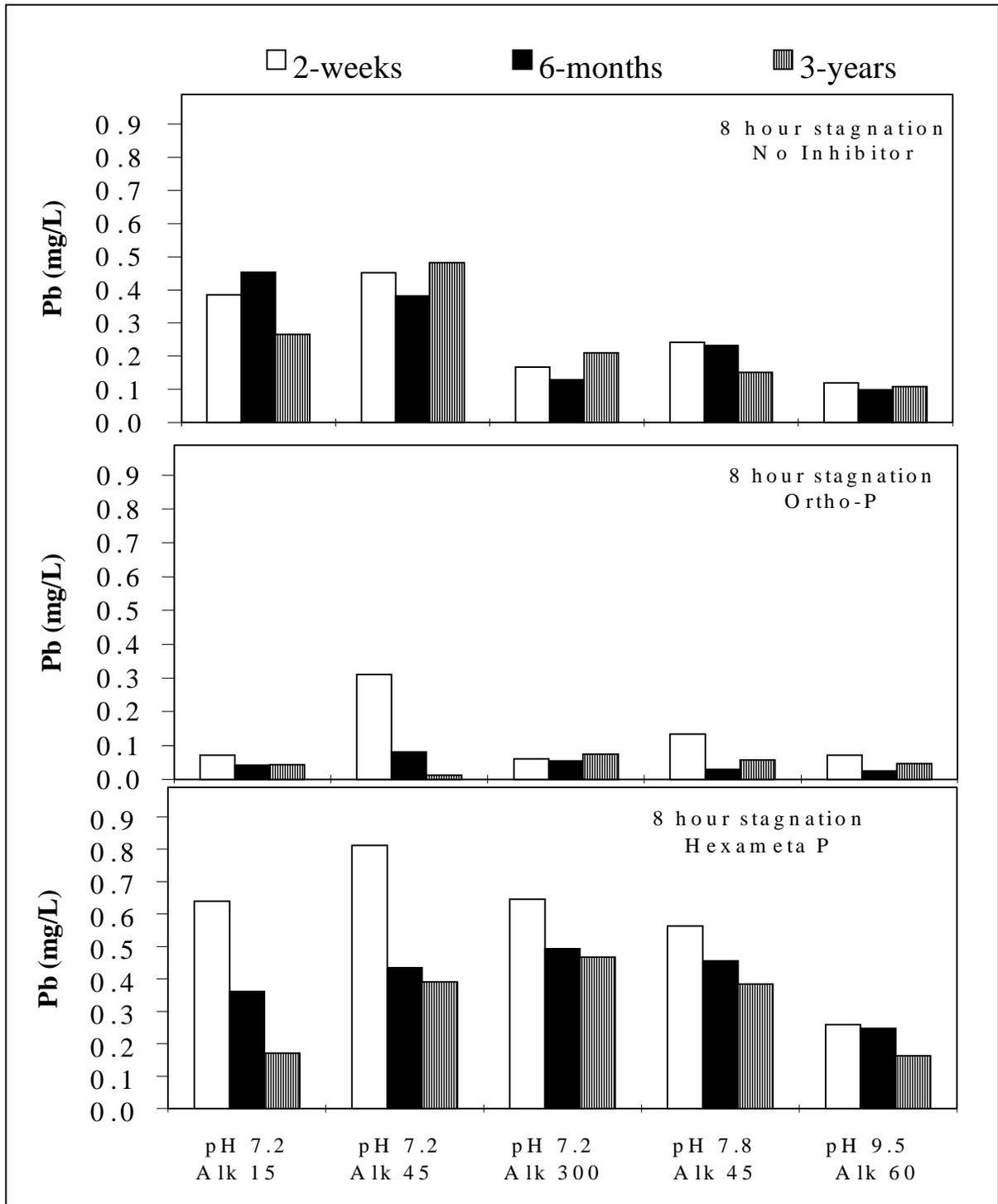


Figure 5-10. Soluble lead release in the 8-hour stagnation sampling event.

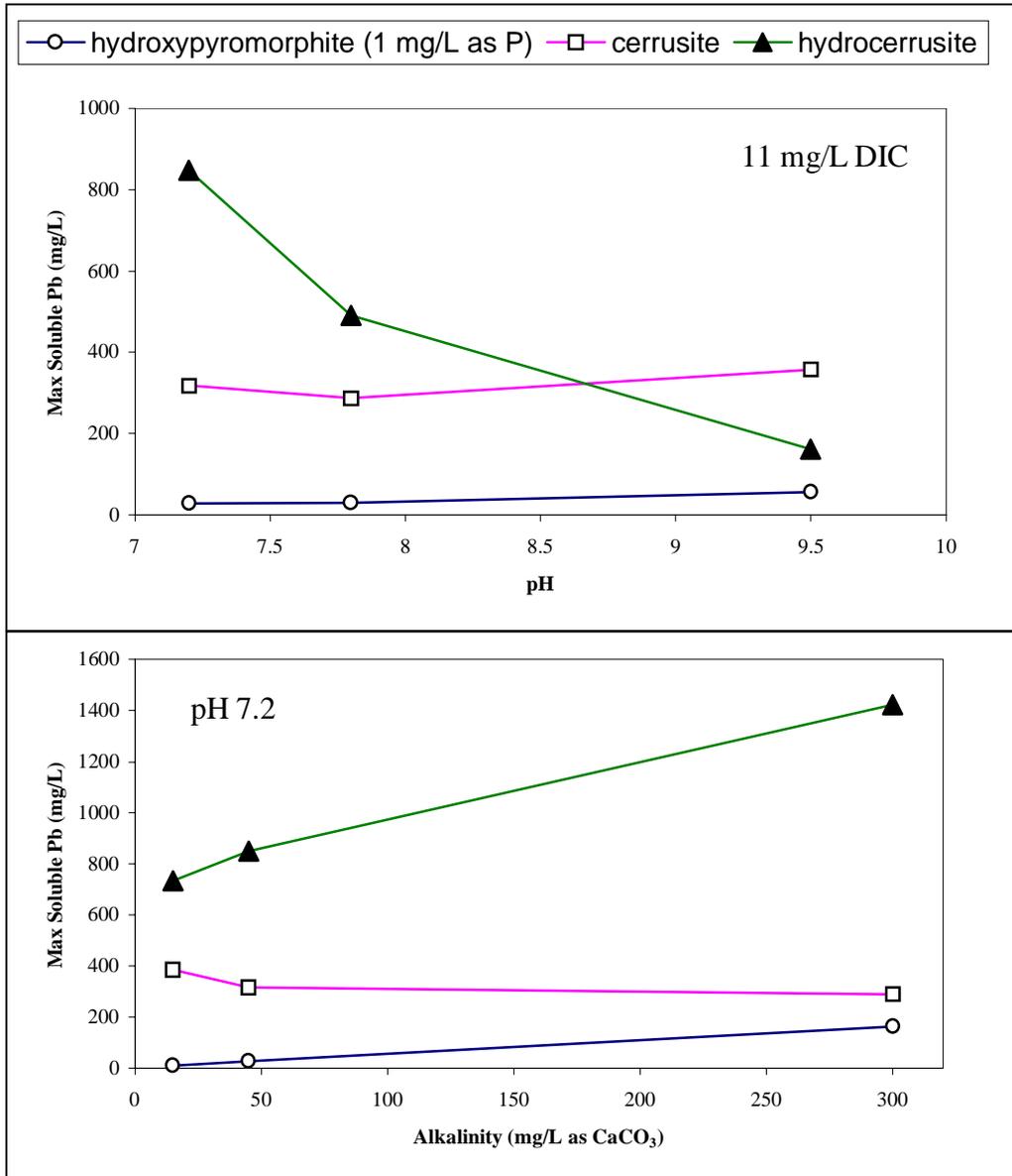


Figure 5-11. Predicted soluble lead concentrations in equilibrium with different solid phases at constant DIC (upper graph) and pH (lower graph).

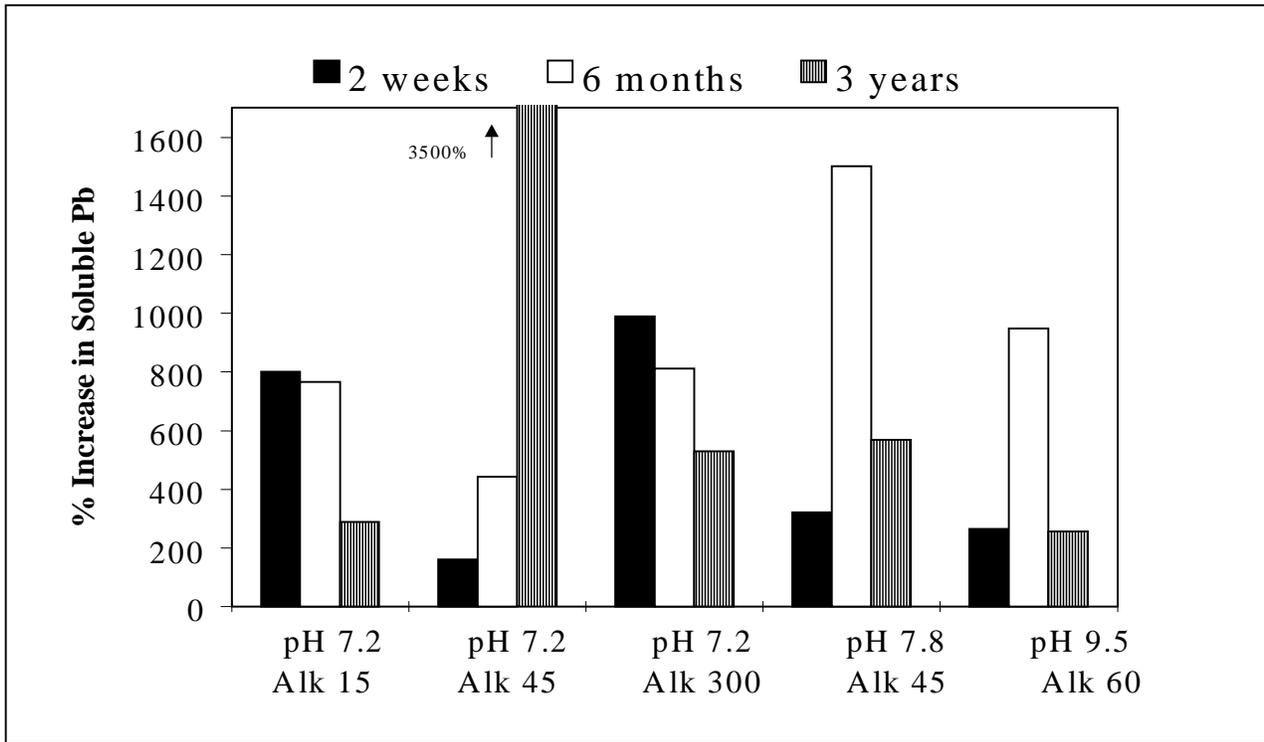


Figure 5-12. Percentage increase in soluble lead due to use of hexametaphosphate compared to orthophosphate.

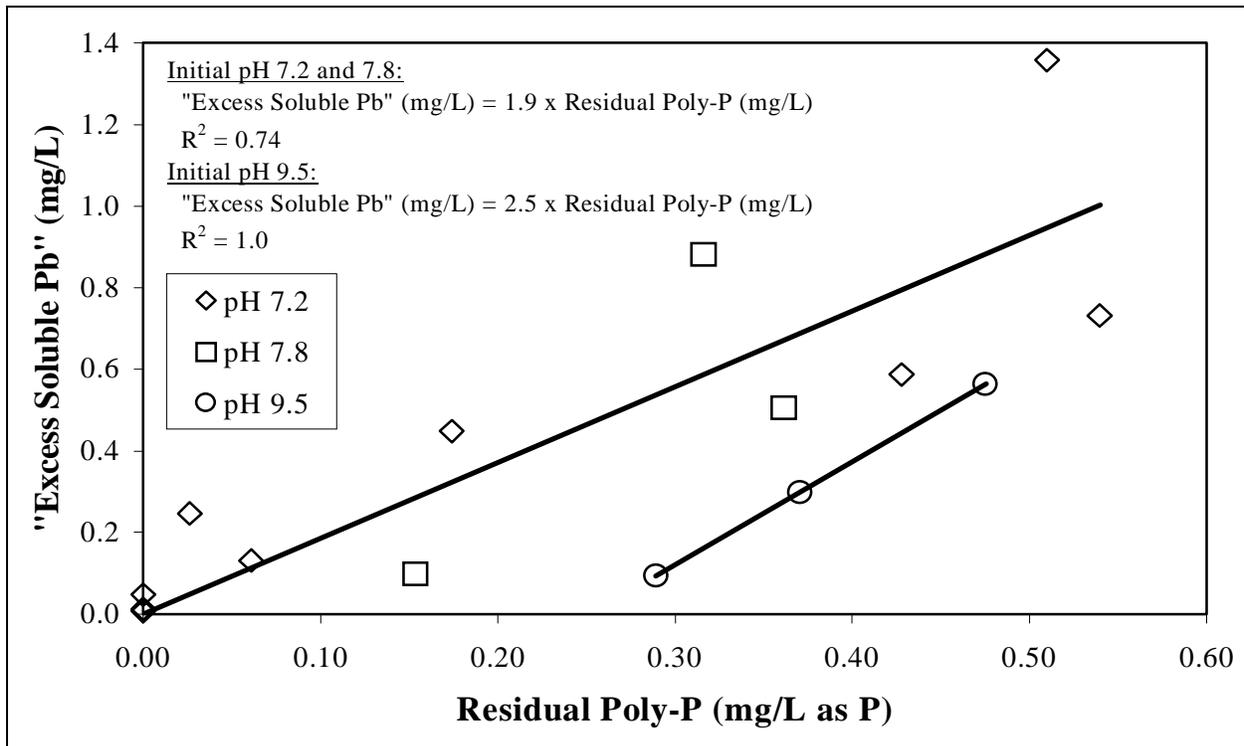


Figure 5-13. Excess soluble lead as a function of residual hexametaphosphate for all pipe ages and pH conditions, 72 hour stagnation.