Coupon Procedures for Evaluating Lead and Copper Solubility

David A. Cornwell and Jacob R. Wagner

Key Takeaways

Coupons have been used to evaluate corrosion in pipes since before the Lead and Copper Rule was enacted; there's a new way to conduct coupon studies.

Tests using coupon protocol can provide reproduceable data quickly and cost-effectively.

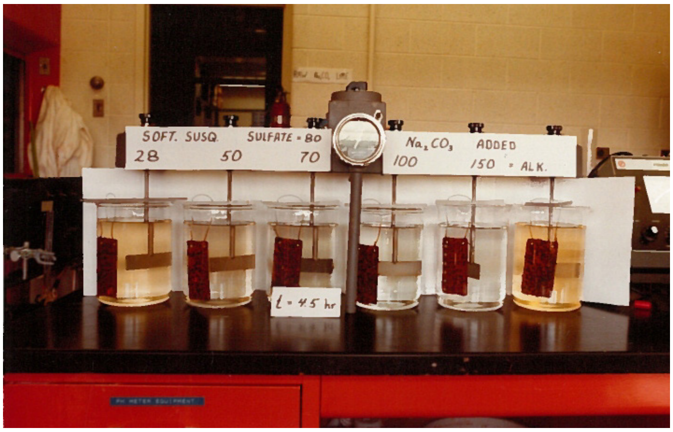
Coupon studies have their limitations, but when used and interpreted correctly, they're useful in multivariable analysis.

Layout imagery by Shutterstock.com/l i g h t p o e t, AlenKadr, streetlucifer

It has been 28 years since the Lead and Copper Rule (LCR) was enacted (56 FR 26460–26564, June 7, 1991), and the US Environmental Protection Agency is now working on an update. The original rule and associated guidance provided methods for utilities to evaluate lead and copper levels and control measures in their distribution system. The process of performing those evaluations is referred to as a corrosion control study (CCS). The results of a CCS are used to identify which corrosion control treatment (CCT) a utility would be required to implement. Small systems generally could complete a CCS by doing a "desktop" study or by finding similar systems that already had effective corrosion control and copying their CCT method. Larger systems (serving a population greater than 50,000) were required to conduct a demonstration study, with the goal of minimizing lead and copper within other water quality and regulatory constraints.

There are three acceptable methods for a demonstration CCS: full-scale testing in a defined portion of the distribution system, coupon studies, and pipe loop studies. Full-scale testing has inherent challenges and limitations, and pipe loop studies are typically used only by very large systems. As discussed in the following, coupon studies were not particularly successful in predicting lead and copper release. Here, we provide a historical review of coupon procedures and presents a new method to conduct coupon studies. We refer only to lead corrosion, but the procedures are equally applicable to copper.

This photograph shows a pipe loop/coupon study.
Source: AWWA 2011, Figure 6-8



A coupon study from the 1970s.

Historical Coupon Procedures

The use of coupons to evaluate corrosion preceded the LCR. The LCR guidance manual (USEPA 1992) included pipe coupon test procedures. Similar to that manual, the AWWA Research Foundation (AwwaRF) published a more detailed discussion of the same basic methodologies in 1996 (AwwaRF 1996).

Coupon procedures described in these documents generally centered on evaluating the weight loss of the coupons during exposure to the water. The coupons were typically purchased from a supplier that would clean and weigh the coupon and place an identification number on it. After the study was complete, the coupon was returned to the supplier to be cleaned and weighed, and the weight loss was reported back to the user. In theory, weight loss for different treatment scenarios could be compared using the weight loss data. Coupon tests could be performed on any metal pipe material, and lead, copper, and mild steel coupons were all readily available.

As stated in the LCR guidance manual, coupon studies generally require long exposure periods before reliable data are available. A 90-day exposure is considered the minimum time required, with many test periods lasting six months. The testing was often done on a flow-through basis, and a common procedure that is still used is to place the coupons in the distribution system piping at an accessible location. Coupons would be rotated in and out of the distribution system for several months. For example, coupons might be left in place for three- or six-month intervals, with new ones put in after removal of the older set. This process is useful for evaluating the CCT in the system, but not for evaluating alternative corrosion control strategies.

Pipe loops can be used to evaluate different treatment conditions, in which coupons are inserted into the flowing loop system. Different CCT methods can be tested using a number of different pipe loops. The left-hand photograph on page 14, from the AWWA Manual of Water Supply Practices M58 (AWWA 2011), shows such a pipe loop/coupon study, which requires this type of coupon setup.

As reported in AwwaRF's 1996 report, "a major drawback to the coupon weight loss analysis has been the high degree of variation between individual measurements, which has limited both the application and the acceptance of the technique." In evaluating the way these studies had been done, it is apparent that one of the problems with those corrosion coupon tests was that only the total weight loss was calculated. That same report indicated that it would take 10 replicate coupons to achieve 10% precision.

However, the rate of corrosion, and hence metal loss, is greatest at the beginning of a test and then levels off as the coupon becomes conditioned. Different CCT methods might have higher initial metal loss, but it could level off at lower levels than another method with lower initial losses. Since lead pipes have been in distribution systems for many years, it is the equilibrated lead values and associated weight loss that are important. It's difficult to separate the initial weight loss from the equilibrated lead weight loss without an extensive number of coupons being analyzed over time. In essence, these coupon test methods didn't have significant advantages over pipe loop studies, and in fact may have had more disadvantages.

Researchers began trying static coupon methods for testing lead, iron, and copper corrosion in an attempt to shorten the study period. In fact, in the late 1970s, one of us (DAC) tested short-term static methods for iron corrosion, as shown in the right-hand photograph on page 14. In those studies, coupons were placed in jar test equipment for a few days, and iron color was observed for different alkalinity levels. This was a rudimentary test, but it was helpful to quickly screen alternatives.

Patterson and O'Brien (1979) used static coupons to test pH, alkalinity, and orthophosphate on lead release. In those studies, the waters were adjusted and coupons were exposed for 30 days. Lead measurements were collected after nine and 30 days. Over the years, Edwards and colleagues have reported on their use of static coupon testing, and one can see an evolution in those procedures. Edwards and Ferguson (1993) inserted copper coupons into 500-mL glass jars with 400 mL of solution inside.

Cornwell Coupon Protocol

Water preparation

- Determine conditions in the distribution system to establish and use for testing.
- Collect water from the finished water source, noting that if different inhibitors are to be tested, the sample needs to be collected prior to inhibitor addition.
- For baseline conditions, set the pH and disinfectant residuals by representative values in the distribution system. Establish additions to be made to provide corrosion control treatment—for example, pH change, alkalinity change, phosphate addition. Final pH may need to be adjusted after these additions.
- Prepare duplicate jars whenever possible.

Testing

- Adjust the primary variables each time the water is replaced in the coupon jar: pH, chlorine or chloramine residual, and the inhibitor type and dose.
- Change test water twice per week by preparing a new jar of water and carefully swapping the coupon from the old water to the new water. Use 500-mL containers with the desired coupon material (3 × 0.5 in.) suspended in the water.
- Fill the jar completely such that when the top is put on the jar, a seal is created.
- Check the pH after the three- or four-day holding time. If the pH varies substantially, make sure there is a water-tight seal.
- Acidify the previously stagnating sample in the test container (jar, bottle, etc.), hold for 16 hours and analyze lead.
- Report results as µg/L-day.

Figure 1

Example Coupon Test Setup

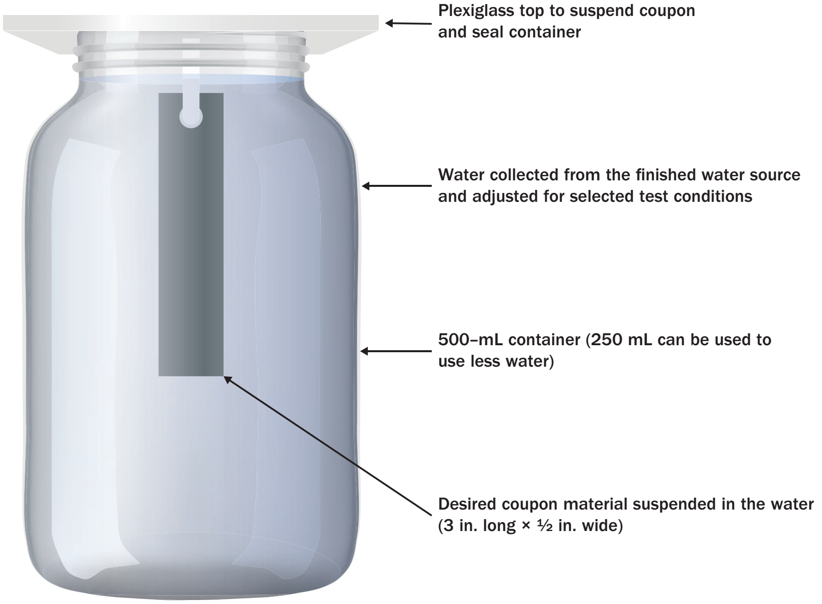


Figure 2

The water was exchanged every third day. Edwards and Triantafyllidou (2007), in studying chloride-to-sulfate mass ratio, epoxied coupons to the bottom of 46-mL open-top glass vials. The water was changed three times per week. The studies lasted approximately 11 weeks, with metals analyzed weekly. Nguyen et al. (2011) placed coupons in open-top 100-mL jars and changed the water twice per week. At the end of the week, composite samples were analyzed for lead. This continued until the lead values stabilized, which was about five weeks.

As discussed, successful research has been completed using static coupon tests with a relatively short duration. Despite that, there still has not been widespread use of a static coupon procedure by utilities in assessing CCT. Part of that infrequent use is due to the lack of a uniform test procedure that can provide reliable comparisons of different CCT methods.

Development of a Standard Coupon Protocol for LCR Studies

A standard protocol for coupon tests should achieve several goals:

- Provide a semi-quantitative evaluation of different CCT methods; the method should be relatively quick, inexpensive, and provide for screening of alternatives.
- Estimate whether a given CCT will provide improvement over an existing CCT.
- Provide relative performance of different CCT methods.
- Help establish a pipe loop testing plan, when needed, by quickly screening alternatives.
- Allow for a variety of materials to be tested.
- Simulate water quality conditions in the distribution system as closely as possible.

It's important to interpret the results of coupon studies with a knowledge of corrosion theory such that the test results are not accepted without a reality check against theory or experience. Every coupon study has inherent limitations, and the results for metal testing should not be considered a predictor of lead levels in the distribution system. Relative comparisons of different strategies can be made, but absolute results are not obtained. As mentioned previously, sometimes judgment has to overrule illogical results. As with any multivariable experiment, outliers occur and sometimes the results lie outside the bounds of reason.

Finally, it is important to remember that coupon testing cannot simulate the pipe scale buildup that occurs in the distribution system over many years. While short-duration coupon tests can develop crystalline scales, those scales are not the same as the often-complex scales formed over many years in distribution system pipes. Coupling pipe-scale analysis with coupon studies is an ideal method to better understand the system and determine whether pipe loops are needed after the coupon study. Coupon studies alone cannot predict by whether a change in CCT will disrupt existing pipe scales.

Coupon Protocol

The Cornwell coupon protocol (CCP) has characteristics similar to those reported but has been improved to provide comparative and repeatable results. The

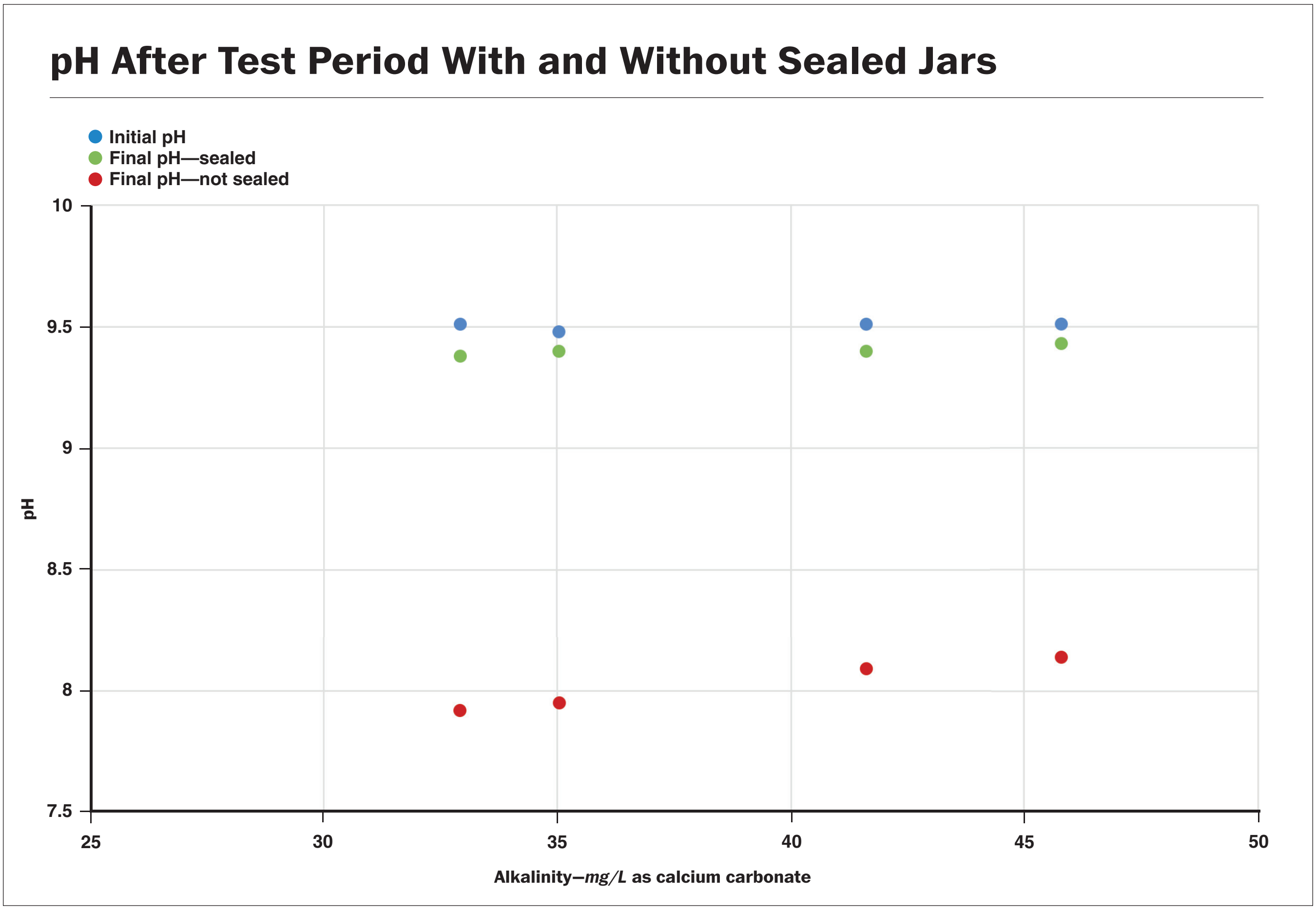


Figure 3

following sections describe the methodology (illustrated in Figure 1).

Water Preparation

Whatever conditions are anticipated in the distribution system need to be established and used for testing. Water can be collected from the finished water source, noting that if different inhibitors are to be tested, the sample needs to be collected before inhibitor addition. Primary variables must be adjusted each time the water is replaced in the coupons: pH, chlorine or chloramine residual, and the inhibitor type and dose.

For baseline conditions, the pH and disinfectant residuals are generally set by representative values in the distribution system. If pH varies significantly in the system, high and low values might be selected for testing. In addition to pH and disinfectant residual, any parameters of interest are also adjusted for comparisons (e.g., alkalinity). Different inhibitors are often tested at different doses, so those products need to be added to the water at the appropriate concentrations.

The general procedure requires that each day the water is replaced in the coupon jars, adjustments must first be made to the test water. The disinfectant residual is adjusted by adding free chlorine and, if needed, ammonia. Alkalinity adjustments, if any, are made; inhibitors are added; and finally, the pH is adjusted to the desired value. This water preparation is the most time-consuming part of the testing.

Testing

Various configurations can be used, but it is convenient to use 500-mL containers, with the desired coupon material suspended in the water. Testing can also be done using 250-mL bottles to use less water. The coupons are 3 in.

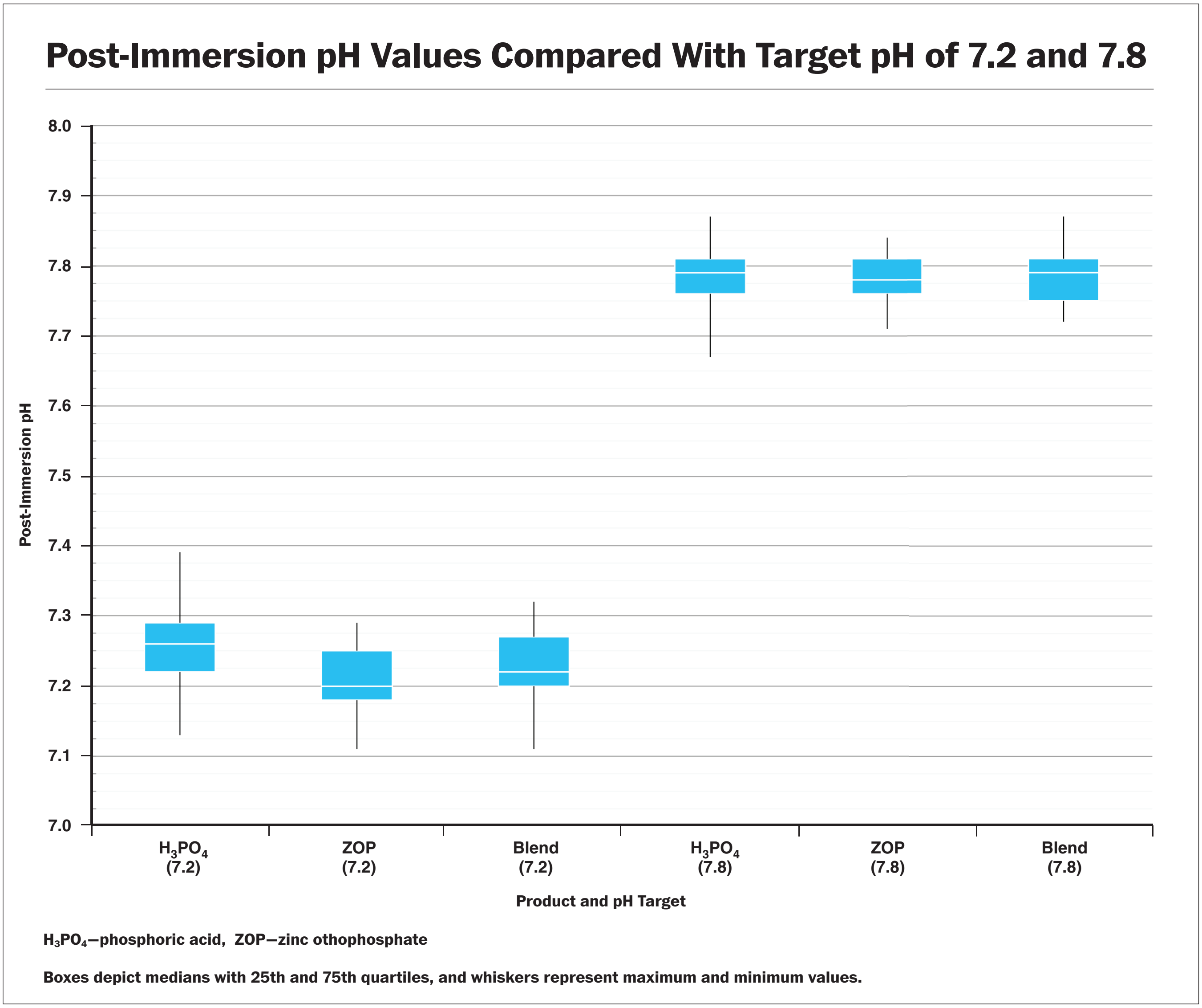


Figure 4

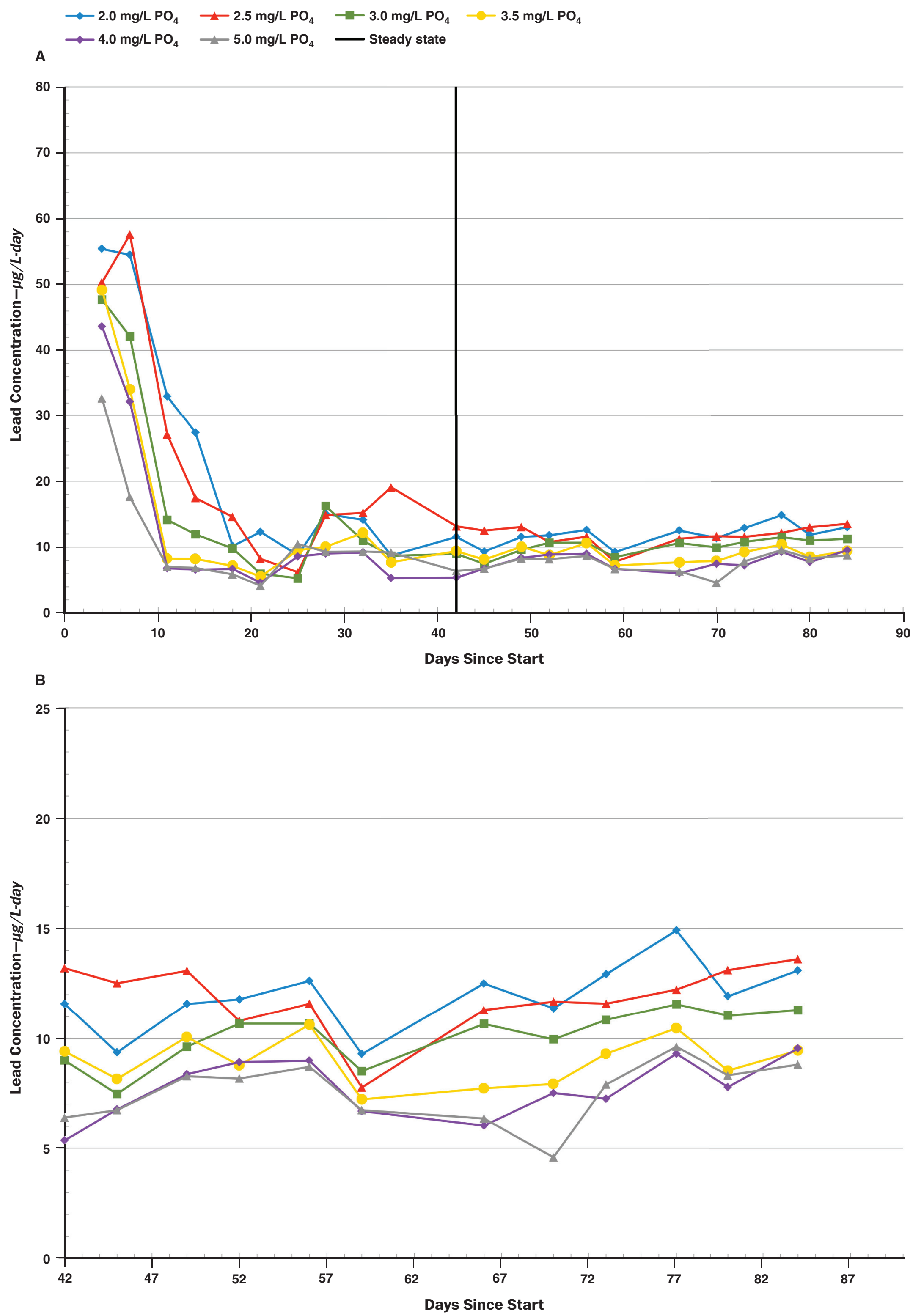
long and ½ in. wide. The resulting ratio of lead surface area to water volume is on the order of 10 times less than an actual lead pipe. But as will be shown, the resulting lead levels are in measurable ranges, allowing for comparisons.

The test water is changed twice per week by preparing a new jar of water and carefully moving the coupon from the old water to the new water. The old jar is acidified in situ with 1:1 nitric acid to below pH 2, held for 16 hours, and an aliquot is removed for metal analysis. Figure 2 shows an example test setup using a 500-mL jar.

It is extremely important to control and check the pH after the three- or four-day holding time. There is always pH drift as a result of corrosion, but if the pH varies substantially from the target, the results may not be representative. This is especially problematic when using low alkalinity or poorly buffered waters exposed to the atmosphere or with headspace in the container.

Figure 3 is an example of the pH after holding for the three- or four-day period. In this case the target pH was 9.5. The blue dots are the pH before the test started and after the water was adjusted to the target pH, and the red dots are the pH after

Example Coupon Results for Different Orthophosphate Dose

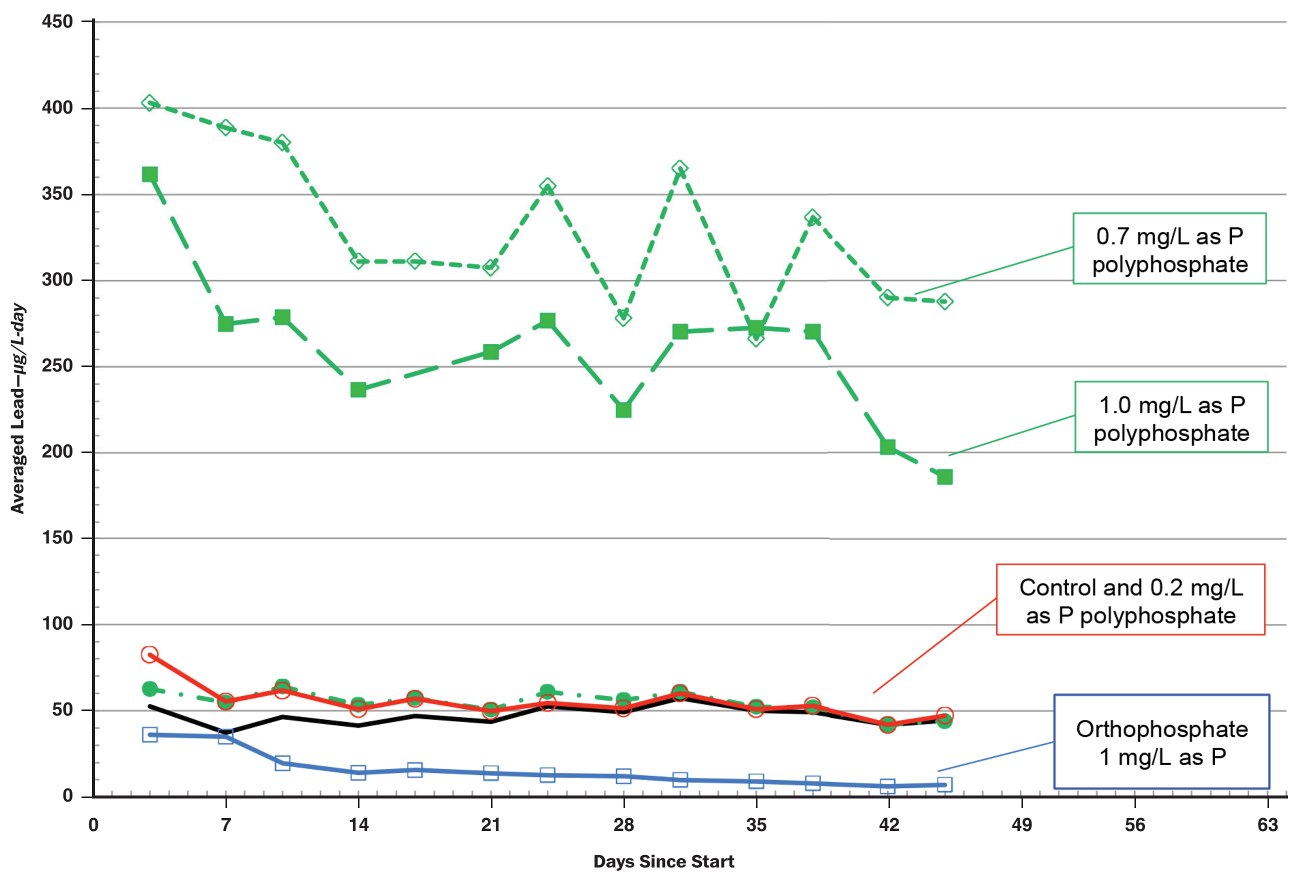


PO_4—phosphate

All results (A) and only steady-state results on a magnified y-axis (B)

Figure 5

Coupon Study Comparing a Polyphosphate With an Orthophosphate



P—phosphorus

Figure 6

testing with open-headspace jars. Clearly, those data would not be representative of a CCT using pH 9.5 as the pH drifted to ~8. The green dots are the same tests but using headspace-free jars. In this case there was no significant pH drift. Figure 4 is another example in which the pH was maintained at two target levels (7.2 and 7.8) using headspace-free jars.

Example Results

This procedure has been used to test lead, copper, mild steel, and brass coupons. Nearly all CCT methods have been tested for various utilities, including mid-8 pH/various alkalinities, high pH/low alkalinity, polyphosphates, blended phosphates, and orthophosphates with different zinc ratios. A common comparison is different orthophosphate doses. Testing has been done to compare with and without granular activated carbon, aeration, ion exchange, and coagulant change and blending scenarios. An example of blending tests was published by Roth and colleagues (2018).

A typical case is to use coupon studies to compare orthophosphate doses. Figure 5 is such an example, showing all the results (part A) and only the steady-state results on a magnified y-axis (part B). Most tests last four to six weeks, but this test was intentionally conducted longer.

To even out the data for the different stagnation times, the lead data are divided by the number of stagnant days, usually three or four, resulting in units of concentration per day. It is easy to see in Figure 5 that the lower doses of orthophosphate (2.0, 2.5, 3.0 mg/L as PO_4) had a slightly higher lead concentration than the higher doses (3.5, 4.0, 5.0 mg/L as PO_4) that were all about the same.

Figure 6 compares the performance of no inhibitor addition with addition of a polyphosphate and an orthophosphate (phosphoric acid). These tests followed a more typical test period than that shown in Figure 5, lasting six weeks. In this case, the polyphosphate at this dose did not perform as well as the orthophosphate product. In fact, it had higher lead than the control, without any chemical addition except for the lowest dose. This is not to say a polyphosphate always has higher lead levels than an orthophosphate, but in this water quality and polyphosphate type it did.

When making comparisons, it is often convenient to use a dot plot approach in which the data, including duplicates, are plotted for different conditions. Figure 7 is a dot plot comparing the performance of different orthophosphate doses. In addition to visual observations, one can apply appropriate statistical procedures to compare the data (Wysock et al. 1995). The coupon studies in Figure 7 were conducted for approximately one year, with the data in Figure 7, part A, representing the results from day 28 to 49, which is a typical period for the coupons to reach steady state and after which time a decision based on the coupon study would be made. Figure 7, part B, shows the same coupons after one year of conducting the CCP. After the one year of coupon exposure, the results are lower; that is, the lead values dropped from about 10 to 2 µg/L-day. However, importantly, the conclusions about dose performance had not changed since the beginning. Performance leveled off at around the 3 mg/L PO_4 dose. It is unclear why the 3.5 mg/L dose was slightly high in both cases, but it was only an increase of about 1 µg/L-day. The 4 mg/L PO_4 dose showed improvement over time but again it is only about 1 µg/L-day. Whether the coupon test was run for six weeks or one year, the conclusion that the optimal PO_4 dose was about 3 mg/L did not change.

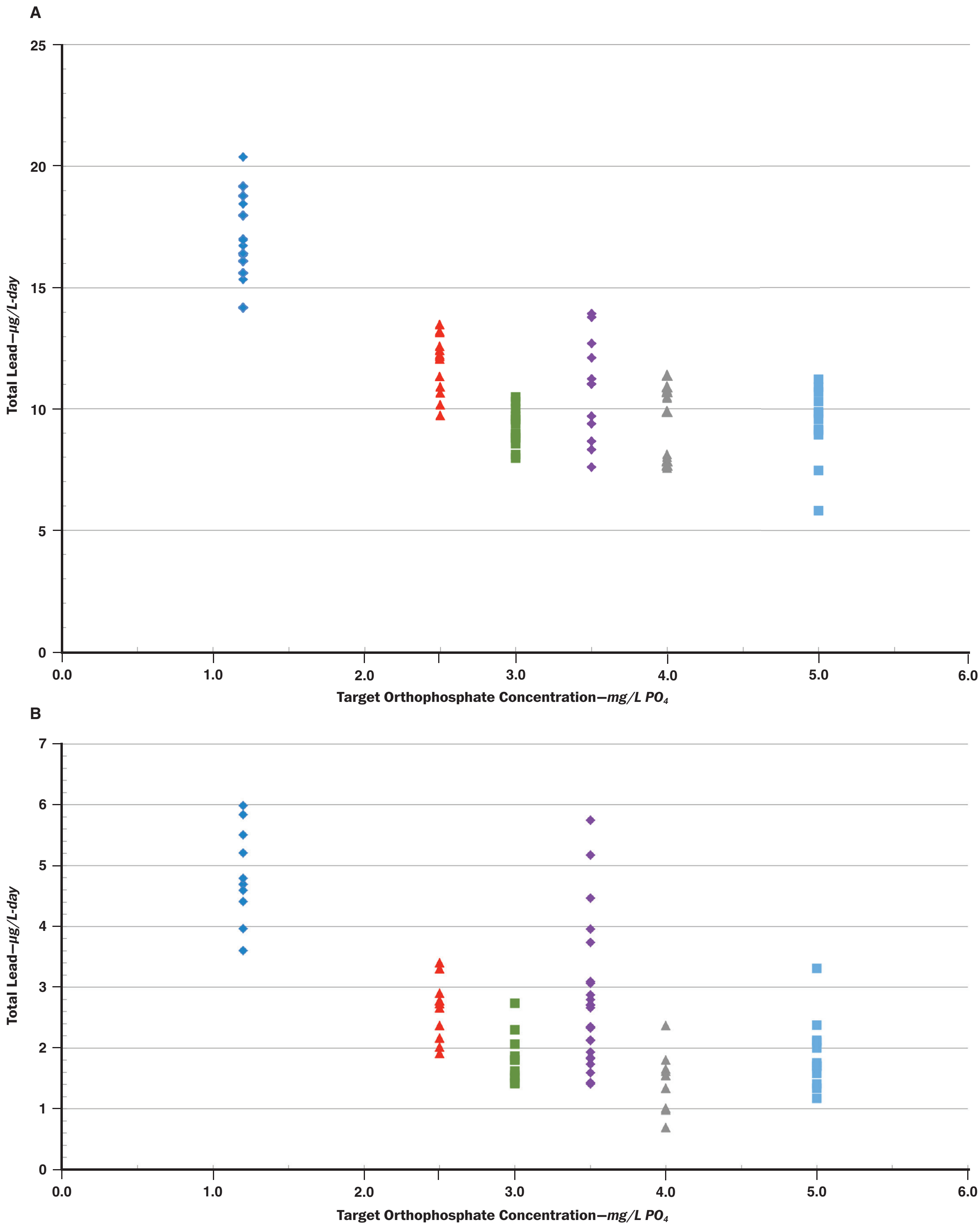
Interestingly, the coupon studies in Figure 7 were conducted on the same water and side-by-side with water feeding harvested lead pipe loops. A dot plot for the harvested pipe loops after about 12 months of operation, the same as Figure 7 for the coupons, is shown in Figure 8. To evaluate the performance of different orthophosphate doses for a coupon study versus a pipe loop, compare Figures 7 and 8. Figure 7, part B, and Figure 8 show the same exposure time, while Figure 7, part A, is only the first six weeks of coupon exposure. One could conclude from the coupon study that a dose of 3 mg/L PO_4 dose looks optimal, but the loop study is not as easy to interpret. The loop study shows fairly similar results for the different doses. There are also slight differences for duplicate lead pipes. This difference is apparent in the 2.5 mg/L orthophosphate dose, in which the two groups of green dots are two different pipes. There is a slight reduction in lead and data scatter as the orthophosphate dose increases to the 3 mg/L range, but the differences are very small. Although not confirmed on the pipes in the loop study, lead IV was found in the scales from other lead pipes harvested from the distribution system. It is speculative, but perhaps lead IV in the pipe scales accounts for the lower lead at the lower PO_4, and that lead IV did not develop on the coupons. Taken literally, the coupons may have resulted in selecting a higher orthophosphate dose than the loops. All of this raises the question of what is optimal: Is 1.2 µg/L lead in the loop study (the median at 4 mg/L PO_4) better than 2 µg/L lead (the median at 3 mg/L PO_4), considering all the differences throughout a distribution system (e.g., varying water quality, different lead pipes, and likely different lead pipe scales throughout the system)? Statistics will ultimately be used to try separating differences, but the same question will remain—even if statistically different, is 1.2 really better than 2?

Tests using the corrosion control protocol can provide useful information, much faster and at a lower cost than pipe loop studies.

Refinements Continue

Following the CCP to conduct coupon studies can successfully provide reproduceable data. The water quality conditions need to be established and adjusted before each water changeout, and testing must be done under headspace-free conditions. Twice-per-week water changes have been used through all of our testing, but recently we have been testing daily water changeout and once-per-week changeout, which has initially confirmed that daily water changes are not needed. The once-per-week changeout seems to take longer to equilibrate, but this approach reduces labor for water changeouts. At this point, we still use twice-per-week water changes.

Dot Plot of Coupon Orthophosphate Dose Data

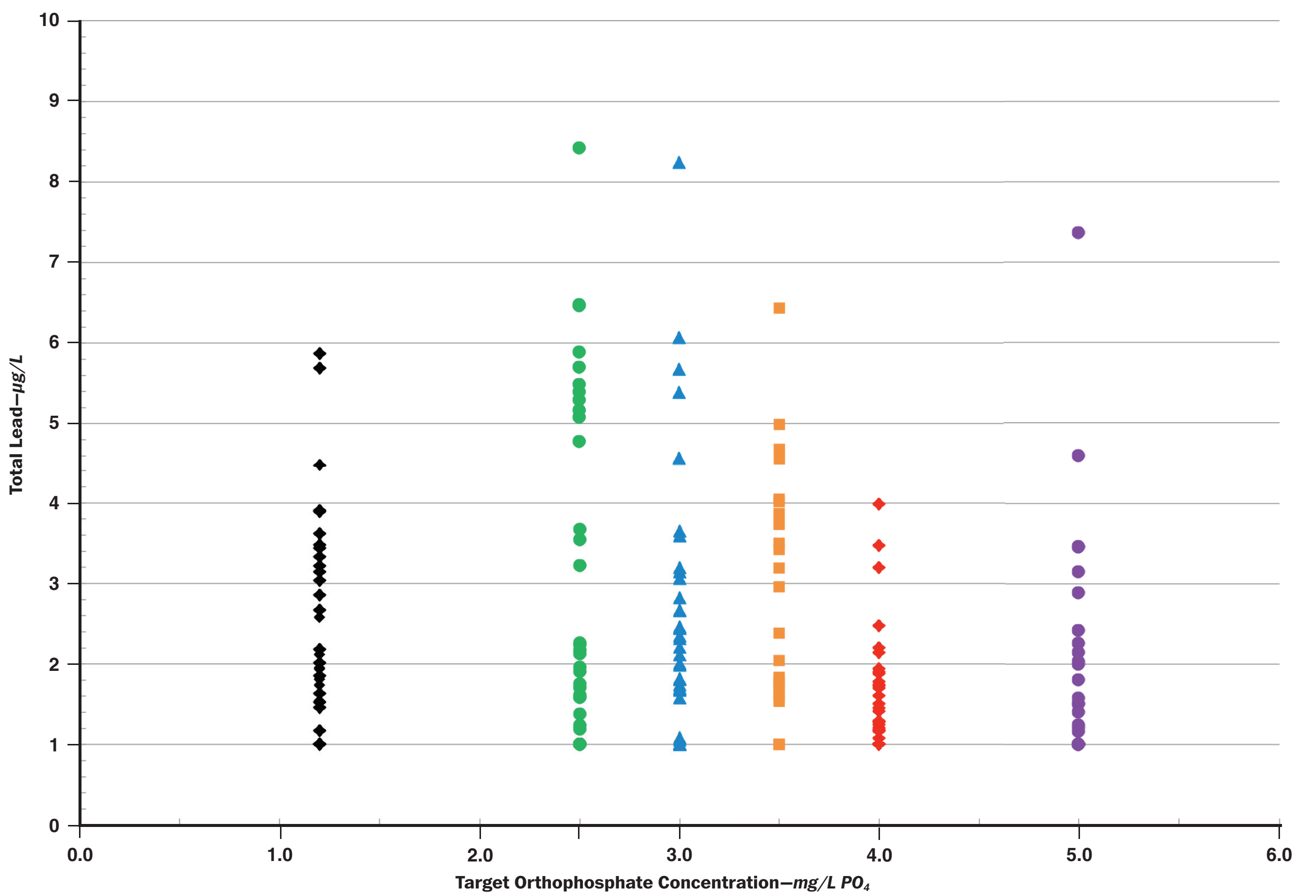


PO_4—phosphate

Data are from day 28 to day 49 since the study started (A) and after 400 days since the start of the study (B).

Figure 7

Pipe Loop Study With Harvested Pipes Alongside Figure 5 Coupon Study



PO_4—phosphate

Same data start date as figure 7, part B (approximately 400 days of loop operation)

Figure 8

Tests using the CCP can provide useful information, and much faster and at a lower cost than pipe loop studies. But coupon study limitations need to be recognized. If scale analysis shows the presence of lead IV, for example, a coupon study would not be appropriate to evaluate lead release when changing from free chlorine to chloramine. Coupon studies also cannot predict changes that could occur to amorphous scales on pipes when CCT is changed. However, when properly used and interpreted, a coupon study can be valuable in evaluating many variables quickly and relatively inexpensively. Again, when the results have been evaluated with an understanding of other variables, the authors have had success in converting utilities' CCT on the basis of the results from coupon studies, often coupled with pipe scale analysis. The methods continue to be refined, but it is hoped that the described protocols can serve as a basis for others to conduct similar studies and further the water industry's understanding of corrosion assessment and control.

About the Authors

David A. Cornwell is chief executive officer of Cornwell Engineering Group Inc. in Newport News, Va.; dcornwell@cornwellinc.com.

Jacob R. Wagner is project engineer at Cornwell Engineering Group Inc.

https://doi.org/10.1002/awwa.1377

REFERENCES

AWWA, 2011 (1st ed.). Manual of Water Supply Practices, M58: *Internal Corrosion Impacts in Drinking Water Distribution Systems.* AWWA, Denver.

AwwaRF, 1996 (2nd ed.). *Internal Corrosion of Water Distribution Systems.* AWWA, Denver.

Edwards, M. & Triantafyllidou, S., 2007. Chloride-to-Sulfate Mass Ratio and Lead Leaching to Water. *Journal AWWA,* 99:7:96. https://doi.org/10.1002/j.1551-8833.2007.tb07984.x.

Edwards, M. & Ferguson, J.F., 1993. Accelerated Testing of Copper Corrosion. *Journal AWWA*, 85:10:105. https://doi.org/10.1002/j.1551-8833.1993.tb06085.x.

Nguyen, C.K.; Stone, K.R.; & Edwards, M.A., 2011. Chloride-to-Sulfate Mass Ratio: Practical Studies in Galvanic Corrosion of Lead Solder. *Journal AWWA,* 103:1:81. https://doi.org/10.1002/j.1551-8833.2011.tb11384.x.

Patterson, J.W. & O'Brien, J.E., 1979. Control of Lead Corrosion. *Journal AWWA,* 71:5:264. https://doi.org/10.1002/j.1551-8833.1979.tb04347.x.

Roth, D.K.; Wagner, J.R.; & Cornwell, D.A., 2018. Impacts of Source Water Blending on Lead Release. *Journal AWWA,* 110:10:15. https://doi.org/10.1002/awwa.1129.

USEPA (US Environmental Protection Agency), 1992. *Lead and Copper Rule Guidance Manual: Volume II: Corrosion Control Treatment.* USEPA Office of Water, Washington.

USEPA, 1991. National Primary Drinking Water Regulations. 40 CFR, Parts 141 and 142. *Federal Register,* 56:110:26460.

Wysock, B.M.; Sandvig, A.M.; Schock, M.R.; Frebis, C.P.; & Prokop, B., 1995. Statistical Procedures for Corrosion Studies. *Journal AWWA,* 87:7:99. https://doi.org/10.1002/j.1551-8833.1995.tb06397.x.