

Harvested versus conditioned new test pieces in drinking water lead or copper corrosion testing

A. F. Cantor ^{a,*}, J. Barry Maynard^b and Andrew Jacque^c

^a Process Research Solutions, LLC, P.O. Box 5593, Madison, WI 53705, USA

^b Corrosion Scales LLC, 2625 NE 16th Ave., Portland, OR 97212, USA

^c Water Quality Investigations, 2581 State Road 92, Suite 2, Mount Horeb, WI 53572, USA

*Corresponding author. E-mail: acantor@processresearch.net

 AFC, 0000-0001-7499-8027

ABSTRACT

Corrosion monitoring apparatuses are important tools in drinking water distribution systems for empirically assessing effectiveness of corrosion treatment before application to the entire water system. They are also important for tracking lead or copper release in the distribution system before, during, and after a treatment strategy is in place. A major debate is whether to use test pieces of pipe harvested from the distribution system or to use conditioned new metal surfaces. Harvested and conditioned new test pieces were studied in multiple types of water systems using analysis of chemical scales, biofilms, and metals release data. It was found that both methods of testing are equally valid if procedures follow certain conditions: (1) apparatus configuration and operation are consistent, (2) properties of distribution system pipe wall accumulations are known, (3) dissolved and particulate metal fractions are determined, and (4) apparatus metal release data are correlated with residential data. The use of conditioned new test pieces, obtainable with relative ease, lowers corrosion control study costs, providing a tool for water systems of all sizes to select the most effective corrosion control strategy and to pro-actively track lead and copper release trends in the distribution system.

Key words: copper, corrosion control treatment study, drinking water quality, lead, lead and copper rule, pipe rig

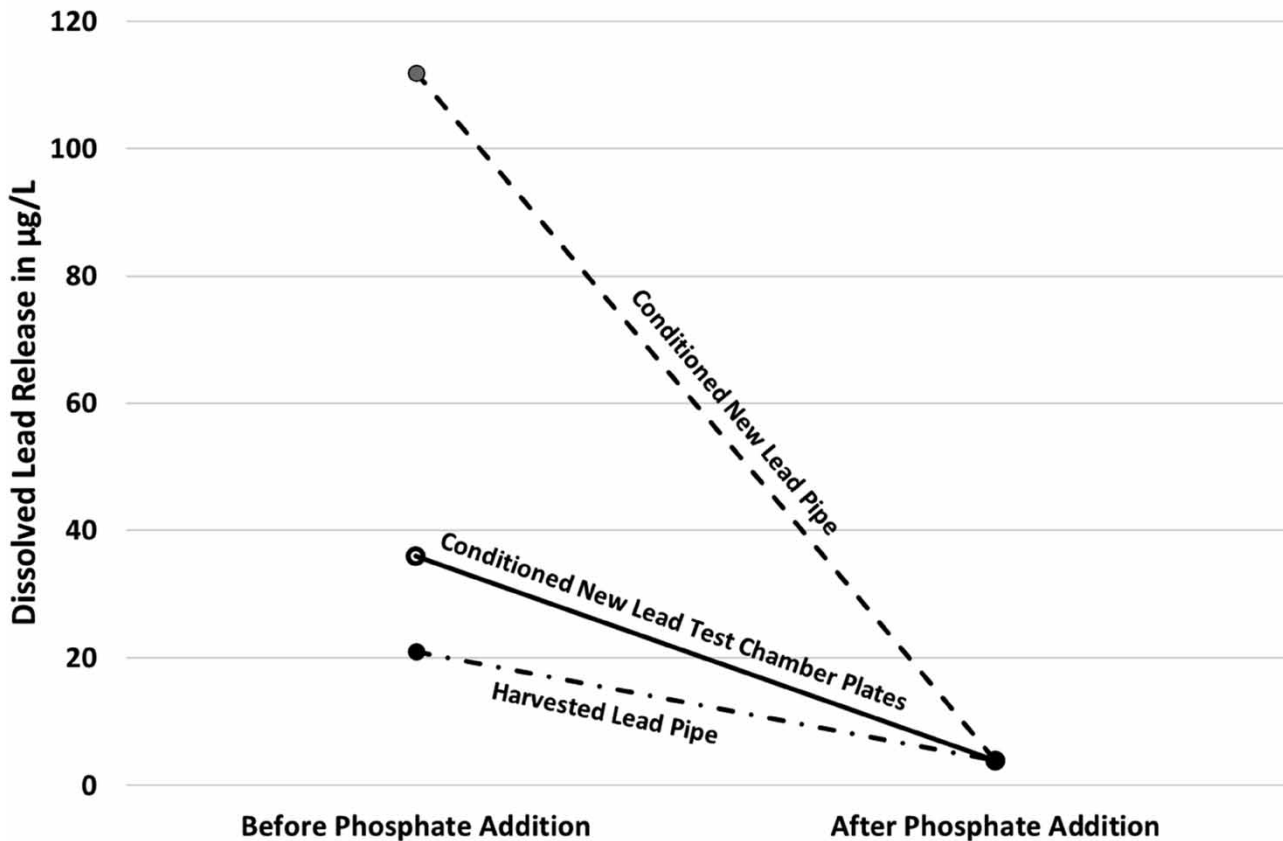
HIGHLIGHTS

- This research demonstrates that data from conditioned new metal test pieces and harvested metal test pieces are equally representative of actual lead and copper release in a drinking water distribution system and equally valid when considering and choosing chemical treatments.
- With either harvested test pieces or conditioned new test pieces, the testing or monitoring program should (1) maintain consistency of apparatus configuration and operation, (2) determine the properties of distribution system pipe wall accumulations, (3) identify metal fractions of the total metal concentration, and (4) place apparatus data in context with residential sampling.

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GRAPHICAL ABSTRACT

Both Harvested and Conditioned New Test Pieces are Valid For Drinking Water Lead or Copper Corrosion Testing



1. INTRODUCTION

Special test apparatuses are used for controlled monitoring of lead and copper concentrations in drinking water. Using these apparatuses, lead and copper release trends in a water system can be tracked, corrosion control treatment scenarios can be compared, and the effectiveness of implementing a corrosion control strategy in a distribution system can be determined (Cantor *et al.* 2012; Williams *et al.* 2018).

A major debate regarding the apparatus configuration is whether to use test pieces of pipe harvested from the distribution system or to use conditioned new metal surfaces.

Harvested pipe has chemical scales and biofilms on the pipe walls that have built up over decades; these pipe wall accumulations are in contact with the drinking water and influence the corrosion and release of lead and copper from the piping material (Schock *et al.* 2014; Williams *et al.* 2018). Harvesting pipe sections in a manner that leaves these accumulations intact and properly wetted is a difficult and expensive process (AWWARF & DVWG 1996; Williams *et al.* 2018). Even if lead service lines are being replaced in a distribution system, there is added expense in hand-digging and hand-cutting harvested pipes (atypical pipe replacement practices) for installation in a testing apparatus. The integrity of pipe wall accumulations may be compromised in this process, biasing the data. In addition, pipe wall accumulations usually vary throughout a distribution system with varying chemical, microbiological, and hydraulic environments (Williams *et al.* 2018) making it difficult to select a relatively small number of pipes for testing that are representative of the complete water system.

In contrast, chemical scales and biofilms, characteristic of the water system under study, develop in 4–8 weeks on clean surfaces of new metal test pieces. After this conditioning phase, all test pieces in an apparatus have accumulations that

developed at the same time in response to the same water system conditions, unlike harvested test pieces. The conditioned new test piece data reflect the release of lead or copper due to the response of metal surfaces to water without being confounded by factors based on differences in pipe wall accumulations. This is a more controlled experiment than with harvested test pieces. In addition, new metal test pieces are obtainable with relative ease and are, therefore, less expensive to obtain than harvested pipe sections. Also, apparatuses can be assembled into a more compact configuration. A smaller, less expensive configuration allows for multiple installations at different locations in a water system for a more encompassing understanding of system water quality dynamics.

There are seven historical configurations of monitoring apparatuses to consider, some using harvested test pieces and some using conditioned new metal:

- The American Water Works Association Research Foundation (AWWARF) pipe rig developed in 1990 was the first standardized apparatus design (EES 1990; Kirmeyer *et al.* 1994). Conditioned new lead and copper pipes were used as test pieces to measure lead and copper concentrations that were released to water as the water cycled between flow-through and stagnating conditions similar to building plumbing.
- Recirculating pipe rigs, with conditioned new metal pipe segments as test pieces, have been used since the 1980s to measure electrochemical parameters of corrosion as well as metal concentration accumulation in the water (Reiber 1991; AWWARF & DVGW 1996; Boyd *et al.* 2012).
- Recirculating pipe rigs with harvested pipe segments as test pieces were used, starting in 2004, to measure lead and copper concentrations that developed in water as it cycled between flowing and stagnating conditions, similar to the AWWARF pipe rig but operated as a batch process with frequent water changes (AWWA 2011).
- The Process Research Solutions (PRS) Monitoring Station was developed in 2006 as a non-proprietary apparatus using stacks of conditioned new metal plates in a test chamber. The ratio of metal surface area to water volume in a test chamber simulates a small diameter pipe, that in turn simulates building plumbing (Cantor 2018). For this apparatus, flow-through and stagnation conditions are exaggerated to estimate the greatest potential of lead and copper release for the water system (Cantor *et al.* 2012).
- The Water Research Foundation (WRF) Project 4317 pipe rig was developed in 2014 using specific conditioned new metal piping components characteristic of building plumbing (Parks *et al.* 2014). Flow characteristics of building plumbing were also incorporated into the apparatus operational protocols.
- Since 1990, the AWWARF pipe rig configuration has been used with harvested pipe test pieces in numerous corrosion control investigations. An example of this usage was presented in an article describing an investigation in Flint, Michigan (Williams *et al.* 2018).
- There has been a long history of a batch jar test version of the AWWARF pipe rig operation using new metal test pieces that are not necessarily conditioned. Renewed interest in this coupon immersion method was shown in two 2019 papers (Cornwell & Wagner 2019; Hazen & Sawyer 2019).

All of the apparatus configurations simulate building plumbing using various strategies; all of the configurations have inherited the basic operational characteristics of the original AWWARF pipe rig. Even though the apparatuses differ in test piece ratio of metal surface area to water volume, apparatus operations parameters, and sampling requirements, they represent the use of either harvested test pieces versus conditioned new test pieces.

This research compared the characteristics and performance of harvested to conditioned new test pieces to determine if the two methods are equally valid for empirical testing and monitoring of lead or copper release in a water distribution system.

2. METHODS

2.1. Testing apparatuses

Data from the seven apparatus configurations described above were utilized in this comparative study. Photos and diagrams of the apparatuses can be viewed in the references cited.

As stated previously, all the apparatuses are, essentially, modifications of the original AWWARF pipe rig concept. That is, an electrically-actuated valve controlled by a timer that allows water to enter a plastic housing. The water comes in contact with metal test pieces and periodically is allowed to stagnate adjacent to the test piece surfaces. The water is then withdrawn as a stagnation sample and tested for lead or copper concentration. The cycle of water flow, stagnation, and sampling is

repeated over time, with projects lasting from 6 months to several years. One exception is the coupon immersion method, which is a manual jar test representation of this process and is typically carried out over a short time, on the order of 6 weeks.

Data used in this research were from water quality projects carried out by one of the authors (Cantor) from 1990 to 2020 unless noted as originating from published articles. Table 1 displays the sources of apparatus data used in this paper.

Table 1 also shows that residential building plumbing data were available in seven projects where residential sampling was performed while a PRS Monitoring Station operated in the same distribution system. Residential lead and copper release data came from two sources: (1) the maximum concentration found in an American regulatory compliance sampling dataset and (2) the maximum concentration from profile sampling in individual residences. Regulatory compliance sampling for this study involved obtaining a 1-L first-draw sample of water that had stagnated in building plumbing for 6 h or more for at least 30 residences in each water system (US EPA 2021). First-draw sampling does not capture the highest lead concentration released from a lead service line upstream of the kitchen faucet but is close or equal to the highest concentration for copper release. In this study, the maximum lead or copper concentration in each sampling dataset was used for comparison to apparatus metals release data. Profile sampling is a method of measuring metals release in a residence where successive litres of stagnating water are taken to 'map' lead or copper release from the kitchen faucet, through the building plumbing, and through the

Table 1 | Apparatus data available for comparison

| Data source ID | Authors involved in project | Description | Apparatuses |
|-------------------------------|-----------------------------|--|---|
| GW FC 1 | Yes | Groundwater (GW) system using free chlorine (FC) disinfection | PRS Monitoring Station; building plumbing data |
| GW FC 2 | Yes | Groundwater system using free chlorine disinfection | Coupon immersion testing; AWWARF-type pipe rig with new pipes; AWWARF-type pipe rig with harvested pipes |
| GW FC 3 | Yes | Groundwater system using free chlorine disinfection | PRS Monitoring Station |
| GW FC 4 | Yes | Groundwater system using free chlorine disinfection | PRS Monitoring Station |
| GW FC 8 | Yes | Groundwater system using free chlorine disinfection | PRS Monitoring Station; building plumbing data |
| SW Chl 1 | Yes | Surface water (SW) system using chloramine disinfection (Ch 1) | PRS Monitoring Station; building plumbing data |
| SW Chl 2 | Yes | Surface water system using chloramine disinfection | PRS Monitoring Station; building plumbing data |
| SW FC 2 | Yes | Surface water system using free chlorine disinfection | PRS Monitoring Station; WRF Project 4317 pipe rig; building plumbing data |
| SW FC 3 | Yes | Surface water system using free chlorine disinfection | PRS Monitoring Station; building plumbing data |
| SW FC 4 | Yes | Surface water system using free chlorine disinfection | Recirculating pipe rigs with new pipes and harvested pipes; PRS Monitoring Stations; building plumbing data |
| SW FC 5 | Yes | Surface water system using free chlorine disinfection | PRS Monitoring Station |
| EES (1990) | No | Groundwater system using free chlorine disinfection | AWWARF-type pipe rig with new pipes |
| Williams <i>et al.</i> (2018) | No | Surface water system using free chlorine disinfection | AWWARF-type pipe rig with harvested pipes |
| Parks <i>et al.</i> (2014) | No | Surface water system using free chlorine disinfection | WRF Project 4317 pipe rig |
| Cornwell & Wagner (2019) | No | See reference | Coupon immersion testing; AWWARF-type pipe rig with harvested pipes |
| Hazen & Sawyer (2019) | No | See reference | Coupon immersion testing |

service line to the water main (Cornwell & Brown 2015). In this study, the maximum concentration of lead or copper measured in the building plumbing of each profiled residence was used for comparison to apparatus metals release data.

Besides residential data, this paper focuses on the reproducibility of responses between test pieces in the same apparatus and also between apparatuses exposed to the same water at the same time and location.

It is important to note that water quality characteristics of test and system water, such as pH and alkalinity, are not included in the comparison of results. Response of lead and copper release to various water characteristics is beyond the scope of this paper.

2.2. Data analysis

Apparatus lead and copper release data as well as other distribution system water quality data are considered non-parametric time-series data (Wysock *et al.* 1995). Data analytical techniques used for dataset statistics were:

- Calculation of Shewhart statistics and control charts (Wheeler & Chambers 1992; Cantor *et al.* 2012).
- Identification of 'stabilized monitoring data' where initial transitory data from an apparatus during conditioning were eliminated (EES 1990; Wheeler & Chambers 1992; Wysock *et al.* 1995).
- Comparison of results between two monitoring scenarios using the Wilcoxon Rank Sum test (Wysock *et al.* 1995) where a 'W' statistic or a 'z' statistic was used depending on the number of available data points.
- Comparison of data trends between two scenarios using Spearman's rank correlation (Wysock *et al.* 1995).

Estimation of the expected maximum lead or copper release in water system residences relied on the Shewhart calculation of the 'upper control level' (average plus three variation units) using apparatus data from a given time period.

With all calculations, comparative data were taken from the same time periods to account for any seasonal temperature influences on lead and copper release in water systems and monitoring apparatuses. Locations of sampling sites in a water system were also taken into consideration.

2.3. Pipe scale analysis

Harvested pipes from water distribution systems as well as conditioned plates from PRS Monitoring Stations were analyzed for chemical accumulations on the metal surfaces. This was performed by one of the authors (Maynard) using the following procedures:

- Photography at macro scale, 10×, and 30× with a binocular microscope. Curvature of pipe samples was eliminated using a stacked series of photographs and image processing software.
- Measurement of crystalline components using X-ray diffraction with Rietveld refinement of the spectra (Harmon *et al.* 2022).
- Measurement of scale chemistry by X-ray fluorescence and/or inductively coupled plasma followed by mass spectrometry.
- Measurement of localized chemistry using scanning electron microscopy with energy dispersive spectroscopy.

2.4. Biofilm thickness assessment

Conditioned plates from PRS Monitoring Stations were analyzed by one of the authors (Jacque) for microbiological populations within biofilms adhering to the metal surfaces. The conditioned plates were submerged in a lysing agent to release the biofilms into a solution. With the lysing agent solution separated from the metal components, the solution was analyzed for adenosine triphosphate (ATP) concentration, which can be translated to a population estimate of bacteria per unit of metal surface area.

The following relationships were also used:

- Plate surface area = 8 square inches = $0.00516 \times 10^{12} \mu\text{m}^2$
- Bacterial cell density
 - Biofilm density estimate = 40 mg/cm^3 (Rittman & McCarty 2001)
 - Generic bacterial mass estimate = $91 \times 10^{-15} \text{ grams/cell}$ in a stationary phase (Fagerbakke *et al.* 1996)
 - Therefore, bacterial cell density = $0.44 \text{ cell}/\mu\text{m}^3$
- Biofilm thickness estimate in μm = [(bacterial cells on a test plate surface as estimated by ATP analysis)/($0.00516 \times 10^{12} \mu\text{m}^2$)]/($0.44 \text{ cell}/\mu\text{m}^3$)

3. RESULTS AND DISCUSSION

3.1. Comparison of chemical scales in pipe wall accumulations

Conditioned metal plates from PRS Monitoring Station test chambers were analyzed regarding the chemical nature of their surface accumulations at the completion of several projects; harvested pipe scales were analyzed for chemical scale composition from the same and additional distribution systems.

The scales on new metal surfaces develop during the conditioning period and continue maturing toward thermodynamically stable, less soluble compounds throughout the testing. The most familiar example of this chemical maturation process in distribution systems is the ageing of copper precipitates (Lagos *et al.* 2001). The copper ageing progression when sulfate is not significantly present is (1) cuprite (a copper oxide), (2) cupric hydroxide, (3) malachite (a copper carbonate) or tenorite (a copper oxide).

Figure 1 shows three stages of copper compound maturity which were found simultaneously occurring on harvested copper service lines and also on conditioned copper plates from PRS Monitoring Station test chambers. The scale on the harvested service lines was thicker than on the conditioned new plates and had a higher proportion of the less soluble, more thermodynamically mature mineral, malachite.

This mixture of many phases in both the older and younger scales is confirmed by an article (Lagos *et al.* 2001) that reports the same pattern in comparing new to mature copper building plumbing. Higher copper release is expected from the newer surfaces because of a higher presence of exposed copper metal and of more soluble cuprite. But older piping also maintains the more soluble compounds along with the mature, less soluble compounds, narrowing the difference between copper release from conditioned new surfaces versus older.

Regarding the maturation of lead-based compounds, bare lead surfaces exposed to water quickly form a layer of relatively soluble Pb^{2+} oxide, usually litharge but sometimes massicot. This is then followed, commonly, by less soluble lead carbonates (cerussite or hydrocerussite, or in high pH systems, plumbonacrite).

However, certain environmental factors can favor formation of other lead compounds and override the chemical maturation process. For example, if the oxidation/reduction potential is elevated, the highly insoluble Pb^{4+} oxide, plattnerite, can form (Lytle & Schock 2005).

Another phenomenon is seen with the addition of orthophosphate for corrosion control, where highly insoluble lead minerals form on lead pipe walls, including pyromorphite (lead phosphate) and intermediate compounds of lead, calcium, and phosphate called phosphohedyphane (Hopwood *et al.* 2016).

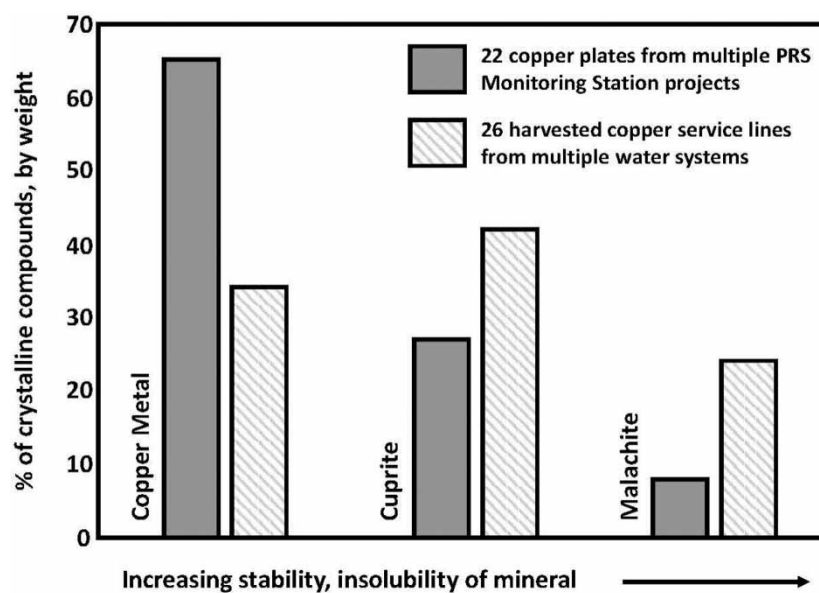


Figure 1 | Mixed thermodynamic maturity of copper compounds on harvested service lines and conditioned new test chamber plates.

Figure 2 summarizes the comparison of mineralogy using chemical scale analyses of conditioned PRS Monitoring Station lead plates versus harvested lead service lines. It was found that lead compounds on harvested lead service lines versus conditioned lead test plates have the same array of minerals, with differences in relative abundances. Lead scales on new surfaces tend to have more of the soluble lead oxides (litharge and massicot) than harvested lead scales. Therefore, higher lead release is expected from conditioned new lead test pieces.

Other features of the comparison shown in Figure 2 are:

- The insoluble lead oxide, plattnerite, did not seem to form significantly on the test plates in the time frame of their deployment as the kinetics of plattnerite reactions are slow (Lytle & Schock 2005).
- The spectrum of lead carbonate phases in the single-layer chemical scales that had formed on the lead plates mimicked a combination of lead carbonate phases in the two layers of chemical scales found on the harvested lead pipes. This similarity indicates that the use of new conditioned lead is a valid model of alkalinity (carbonate) effects, where lead carbonate solubility is a key aspect of lead corrosion (US EPA 2021).
- The phosphate levels in the single-layer chemical scales of the lead plates were similar to the levels in the harvested lead pipe scale that had been adjacent to the water. Therefore, the use of conditioned new lead test pieces is a valid model of orthophosphate effects, where the use of orthophosphate and lead phosphate solubility are key aspects of control of lead corrosion (US EPA 2021).

Additionally, lead release from harvested pipes has also been found in this research to be confounded by existing scales of iron and aluminum on pipe walls. The harvested lead service lines studied in Figure 3 came from various locations in one distribution system and varied in the degree of iron and aluminum scale formation. Figure 3 shows that these scales hinder the rate that a passivating phosphate film can form. Because of the degree of scale variability, harvested pipes as test pieces for an apparatus must be strategically selected.

3.2. Comparison of biofilms in pipe wall accumulations

In addition to chemical scales, naturally-forming biofilms exist on pipe walls and other surfaces in contact with water. Microbiologically influenced corrosion of metals in drinking water systems is a result of chemicals released from microbiological metabolic activity occurring in biofilms on metal surfaces (Gale & Totemeier 2004).

For the context of this research, only the thickness of the biofilm was considered. Oxygen decreases through the thickness of a biofilm from the water interface to the metal surface, and the microbiological metabolisms change from aerobic to

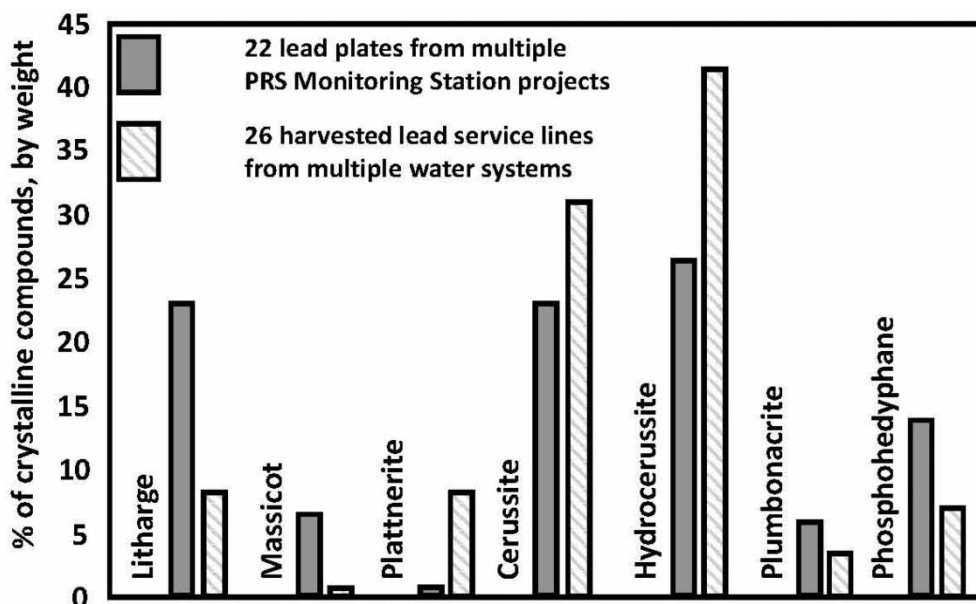


Figure 2 | Mixed thermodynamic maturity of lead compounds on harvested service lines and conditioned new test chamber plates.

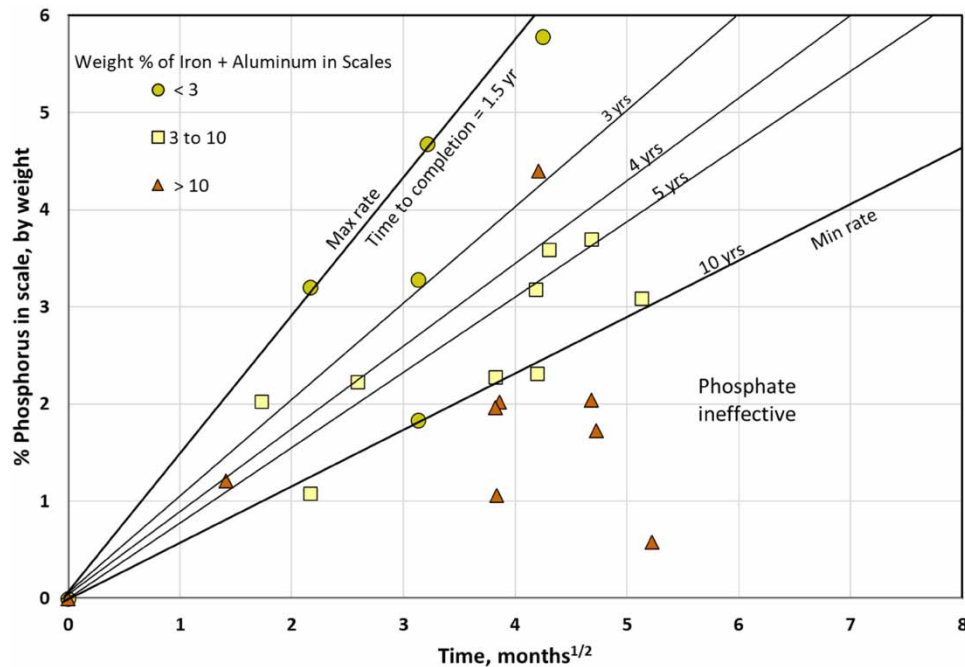


Figure 3 | Interference of passivating phosphate film formation by iron and aluminum scales on pipe walls.

facultative to anaerobic; different metabolisms produce different chemicals and pathways to metals corrosion (Gale & Tote-meier 2004).

Testing of conditioned lead plates from fifteen different PRS Monitoring Station installations estimated a range of bacterial cells per test plate from 3×10^6 to 3×10^9 . The biofilm thickness was calculated to range from less than 0.01 to 1.2 μm with an average thickness of 0.14 μm . Testing of conditioned copper plates from 11 different PRS Monitoring Station installations estimated a range of bacterial cells per test plate from 7×10^6 to 6×10^8 . The biofilm thickness was calculated to range from less than 0.01 to 0.25 μm with an average thickness of 0.09 μm .

In contrast, mature biofilms that can be found in building plumbing can be 3–4 μm thick (Liu *et al.* 2016). Therefore, ‘younger’ biofilms on conditioned PRS Monitoring Station lead and copper plates were thinner with less anaerobic activity than ‘older’ biofilms on harvested pipes.

Particulate metal release from biofilm is a function of the ability of the biofilm to trap and later release corrosion by-products (Rittman & McCarty 2001; Liu *et al.* 2016), the determination of which was outside the scope of this article.

3.3. Representation of the water distribution system

Data for copper and lead release from PRS Monitoring Station test chambers using conditioned new test pieces were compared to residential copper and lead release. The test chamber data average and statistical variation were used to estimate the maximum residential lead or copper release expected in distribution system residences. This number was divided by the maximum observed lead or copper release measured in residences during the same time period for each water system. A ratio less than one indicates that the apparatus underestimated residential metal release; a ratio greater than one indicates an overestimation of residential metal release.

With this analysis, an overestimation of lead or copper release was expected for the PRS Monitoring Station test chambers, not only because of the nature of conditioned new test piece scales, but also because the operation of the apparatus is intended to predict the worst-case lead or copper release for the water system under study by lowering water flow and increasing overall stagnation of water in the test chambers.

For dissolved copper, the copper test chamber estimated dissolved copper release five times higher than the maximum values measured in residences on average. This higher but relatively close relationship of copper release between the copper test chambers and building plumbing was within the expectations set by the analysis of chemical scales shown in

Figure 1. The copper test pieces act similarly to new copper piping in a building (Lagos *et al.* 2001) and represent a worse-case scenario.

Particulate copper release was higher in the test chambers than in residences but was a small fraction of the total copper (dissolved plus particulate copper) concentration. Therefore, total copper comparisons in Figure 4 were similar to the dissolved copper comparisons.

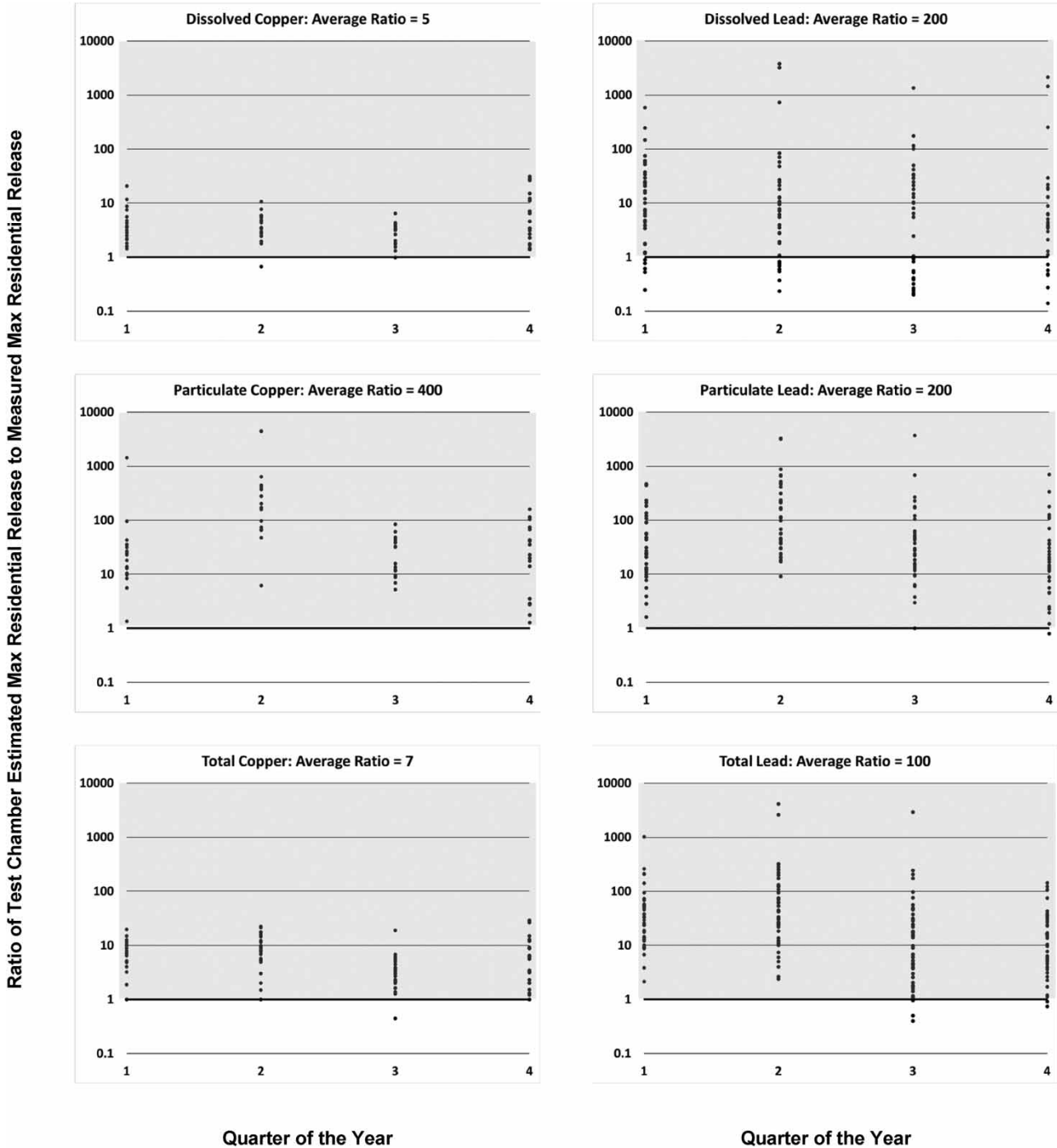


Figure 4 | PRS Monitoring Station test chamber estimate of maximum residential metal release compared to measured maximum results observed in residences during the same time period.

For lead in Figure 4, there were estimates of residential lead release that were over 1,000 times the release measured in residences. Those were special circumstances. One circumstance was when profile sampling was performed in arbitrarily selected residences where maximum residential lead release on the order of 0.01 µg/L (the limit of detection) was compared to test chamber lead release on the order of 10–100 µg/L, calculating to ratios of 1,000–10,000. Another circumstance occurred in one scenario where the apparatus was operating in an urban area during the COVID pandemic when people stopped working from their offices and worked from their residences. There was low water usage at the location of the apparatus coinciding with test chamber particulate lead release at around 3,000 µg/L. This was compared to residences where water usage had increased, and lead release was lower than usual.

For dissolved lead release, the test chamber conditioned new lead test pieces estimated 200 times the observed residential release on average.

Regarding the underestimation of dissolved lead release, it was initially thought that the presence of orthophosphate in a water system may cause lower lead release in test chambers versus in residences. This was based on Figure 2 where the lead/phosphate mineral, phosphohedyphane, formed more easily on the conditioned newer surfaces than on the harvested surfaces. However, the data available in this research did not substantiate that hypothesis.

Particulate lead release from conditioned new surfaces was higher than from residential lead surfaces in the distribution system and was a significant fraction of the total lead release. Particulate lead was overestimated 200 times the observed residential release on average; total lead release was 100 times the observed residential release.

Data from the Flint, Michigan, harvested lead pipe rig (Williams *et al.* 2018) were used to calculate similar comparative ratios between pipe rig data and maximum residential lead release. In this case, data were available from sixteen harvested test pieces after lead release had stabilized. The average-plus-three-standard-deviation values for total lead release from each test piece were available to use in estimating maximum residential lead release. In addition, the article presented the maximum concentrations from profile sampling at two residences. The comparative ratios ranged from 0.14 to 2.54. This falls into a similar range as the PRS Monitoring Stations but on the lower end of the range. These results for the harvested pipe rig data may not only be because of the more mature pipe wall accumulations but also because of the higher water usage in the pipe rig (795 L per day of water per test piece in the harvested pipe rig versus 114 L per day of water per test piece in the PRS Monitoring Station).

3.4. Replication of test pieces

Variability between similar test pieces can be introduced by factors such as alloy composition, test piece fabrication, and amount of metal surface exposed to water (Hazen & Sawyer 2019).

The reproducibility of results between replicate test pieces in apparatuses was studied. Figure 5 identifies the test piece pair results that were statistically similar to each other as determined by the Wilcoxon Rank Sum test. For datasets with less than 25 data points, a ratio of $W_{\text{calculated}}/W_{\text{critical}}$ was calculated, where results between two datasets are statistically similar when the ratio is greater than 1.0. Otherwise, a ratio of $z_{\text{calculated}}/z_{\text{critical}}$ was calculated, where results between two datasets are statistically similar when the absolute value of the ratio is less than 1.0.

It was seen that dissolved copper tended to be reproducible between similar conditioned new test pieces. For dissolved lead, both conditioned new surfaces and harvested surfaces were studied and both types of test pieces appeared to be reproducible in results.

Particulate copper results appeared to be reproducible. Particulate lead results were less likely to be reproducible between similar test pieces, indicating the erratic nature of particulate metals release from surface accumulations.

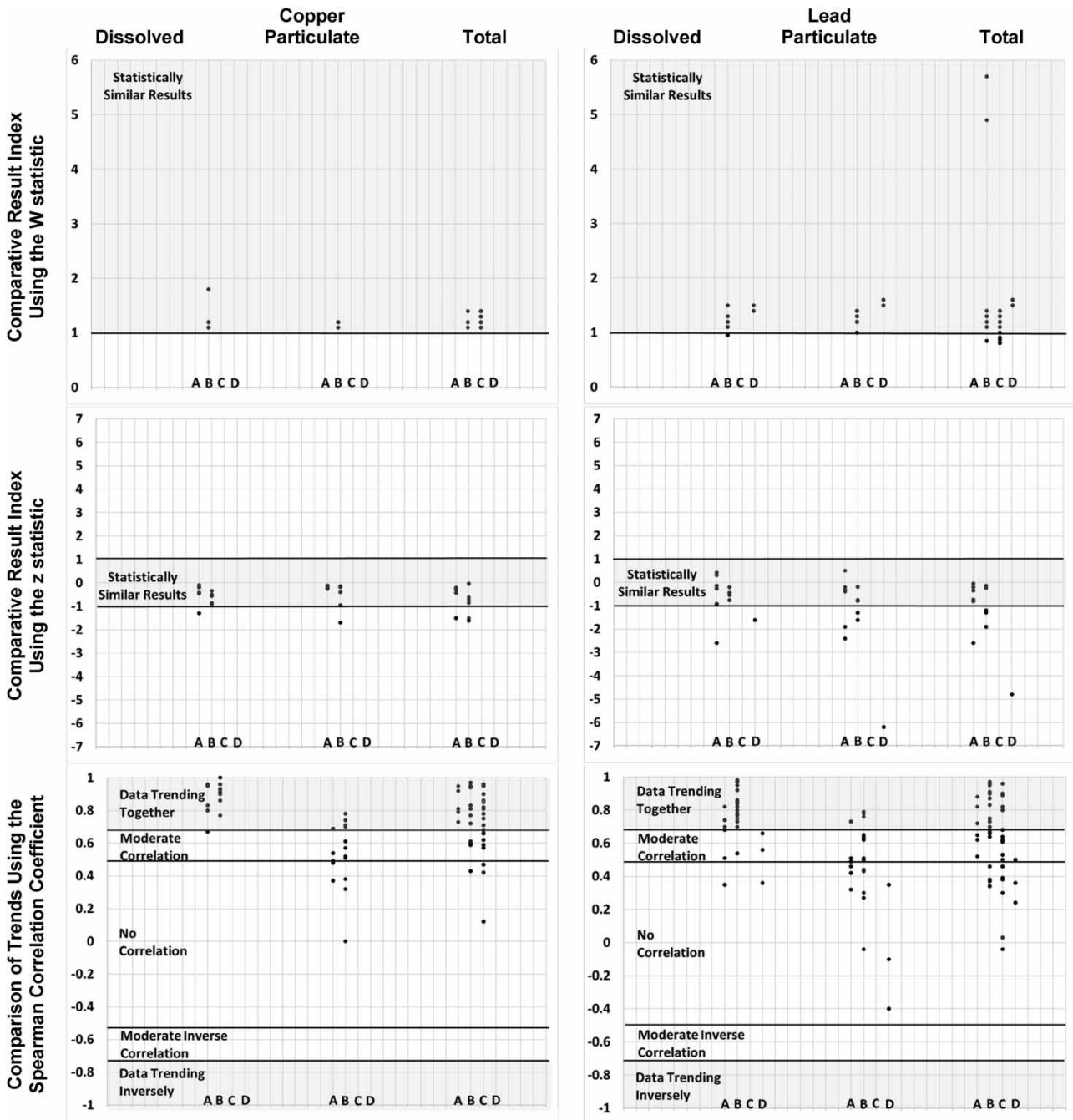
For lead, reproducibility of results was no better or worse for harvested surfaces versus conditioned new surfaces.

Also shown in Figure 5 is a comparison of data trends between pairs of similar test pieces. Trends were compared between datasets using Spearman's rank correlation coefficient, where two datasets have similar trends if the absolute value of the coefficient is between 0.7 and 1.0.

Dissolved copper trends were reproducible between pairs of similar test pieces; dissolved lead trends were 'moderately' reproducible. Both particulate copper and particulate lead release trends did not correlate well between pairs of similar test pieces.

3.5. Comparison of apparatus results

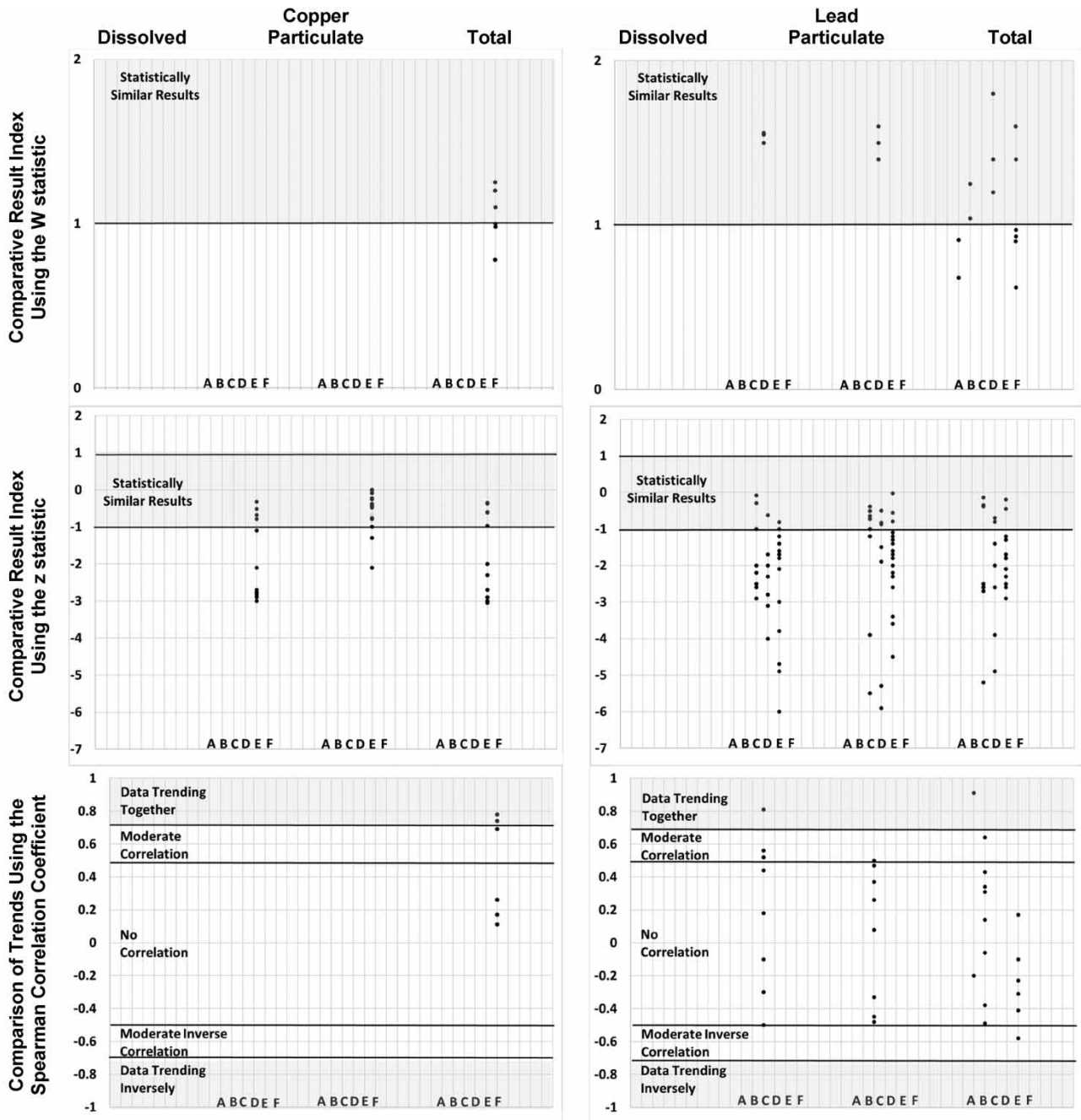
Comparisons were also made of results between pairs of dissimilar test pieces as shown in Figure 6. In all comparisons, there was little similarity of results between pairs of dissimilar test pieces using the Wilcoxon Rank Sum test and little similarity of



A: Recirculating Pipe Rig with Conditioned New Metal
B: PRS Monitoring Station with Conditioned New Metal
C: WRF Project 4317 Pipe Rig with Conditioned New Metal
D: Recirculating Pipe Rig with Harvested Metal

Figure 5 | Replication of test pieces on various monitoring/testing apparatuses.

data trends using the Spearman's rank correlation test. The difficulty in stringently comparing results from different apparatuses is that there are confounding factors based on the configuration and operation of the apparatuses. The release of lead or copper is a function of the surface area of metal exposed to volume of water (EES 1990). Water usage, flowrate, and sampling flowrate also influence the quantity of lead or copper released and captured (Parks *et al.* 2014).



A: AWWARF Pipe Rig with Harvested Metal vs. AWWARF Pipe Rig with Conditioned New Metal
B: AWWARF Pipe Rig with Conditioned New Metal vs. Coupon Immersion Method
C: Recirculating Pipe Rig with Harvested Metal vs. Recirculating Pipe Rig with Conditioned New Metal
D: Recirculating Pipe Rig with Harvested Metal vs. PRS Monitoring Station with Conditioned New Metal
E: Recirculating Pipe Rig with Conditioned New Metal vs. PRS Monitoring Station with Conditioned New Metal
F: PRS Monitoring Station with Conditioned New Metal vs. WRF Project 4317 Pipe Rig with Conditioned New Metal

Figure 6 | Comparison between monitoring/testing apparatus results and trends.

Of special interest were comparisons between conditioned new lead surfaces and harvested lead surfaces (A, C, and D in Figure 6). Seeing no statistical similarities, it was interesting to note that both conditioned new test pieces and harvested test pieces made the same predictions as to which chemical scenario was the best for lowering lead release. For example, in a

project where two harvested lead pipes were used in an AWWARF-type pipe rig to compare no treatment to orthophosphate dosing, the results showed that an average of 22 µg/L total lead release was lowered to an average of 6 µg/L total lead release when orthophosphate was dosed. Two new lead pipes were used at the same time; the results showed that an average of 40 µg/L total lead release was lowered to an average of 4 µg/L total lead release, the same outcome as the harvested pipes.

In another project, untreated versus orthophosphate-dosed scenarios were compared using three types of apparatuses operating in parallel: (1) recirculating pipe rigs with conditioned new lead pipes, (2) recirculating pipe rigs with harvested lead pipes, and (3) PRS Monitoring Stations with conditioned new lead plates. The new pipe test showed a reduction from 112 µg/L dissolved lead release to 4 µg/L; the harvested pipe test showed a reduction from 21 µg/L dissolved lead release to 4 µg/L; the plates in the lead test chambers showed a reduction from 36 µg/L dissolved lead release to 4 µg/L. These were all the same conclusion of significantly lowering lead release with the addition of phosphate.

Another interesting observation involved the nature of the coupon immersion method. With this method, the new test surfaces are typically not conditioned and are exposed immediately to various chemical scenarios. In one project, the immersion tests were performed on new lead coupons comparing untreated water and phosphate-dosed water along with new lead pipes in an AWWARF-type pipe rig. Dosing began before the piping was conditioned. [Figure 6](#), Item B shows that the total lead release was statistically similar between the two methods. The similarity was probably due to the fact that both the coupons and the pipes had new bare surfaces; both tests were performed for only short periods of time and before pipe wall accumulations could be sufficiently established.

In a test described by [Cornwell & Wagner \(2019\)](#), extended coupon immersion results matched harvested pipe results after 400 days. This indicated that, given time, the coupons develop surface chemical scales and biofilms similar to harvested surfaces. That is, the coupon surfaces become conditioned over time. Before the point of conditioning, coupon immersion test results represent an unknown point of scale and metal compound maturity.

4. CONCLUSIONS

There are historically seven configurations of apparatuses for monitoring lead and copper release trends in a drinking water distribution system. Some of these apparatuses utilize harvested test pieces and some utilize conditioned new test pieces. This has led to a debate as to which type of test piece produces valid data for empirical evaluation of corrosion control testing and for tracking metals release in distribution system water. Both sides of the test piece argument agree that metal surface accumulations of chemical scales and biofilms profoundly affect the release of piping metals into the water and are the keys for studying lead and copper release representative of a water system.

Harvested test pieces with legacy scales and biofilms on the metal surfaces are the ideal test condition. However, selecting and procuring harvested pipe segments from the distribution system are difficult to do properly, and it is expensive to hand-dig pipe segments. Any deviation from protocols in pipe segment procurement can impair interpretation of lead and copper release results when these harvested pieces are installed in a testing apparatus.

With conditioned new metal surfaces, the chemical scales and biofilms, characteristic of the water system under study, are developed for all test pieces at the same time; all test piece surfaces begin in a similar condition. This allows for test data reflecting the effect of the system water on lead or copper release as opposed to confounding the data with effects of variable surface accumulations as with the harvested test pieces. The disadvantage of the conditioned new test pieces is that chemical scales and biofilms are 'young' and there are different lead and copper release expectations than for the older accumulations found on harvested test pieces.

However, both younger and older scales are composed of similar compounds with a larger fraction of more soluble compounds in the younger scales ([Figures 1 and 2](#)). The presence of soluble metal compounds translates to higher dissolved metal concentrations released into the adjacent water.

[Figure 4](#) confirms that the estimated maximum copper release for the distribution system using data from conditioned new copper test pieces was higher than maximum copper release measured in residences in the distribution system. Given that the scale comparison between the conditioned new copper test pieces and the harvested test pieces was similar to those described for chemical scales on newer copper building plumbing versus older copper plumbing, the use of conditioned new copper test pieces remains a reasonable and representative estimate of worst-case system copper release.

Regarding lead release, [Figure 4](#) implies that the conditioned new lead plates can greatly overestimate the release of lead in distribution system residences. However, also seen in the data of [Figure 4](#) are many examples where the metals release

estimations were closer to concentrations measured in residences. Therefore, apparatus data should be put in context with distribution system data and inconsistencies should warrant residential investigations. Given the similarity of lead compounds between the scales of conditioned new and harvested test pieces, especially regarding lead carbonates and lead phosphates which are the keys to lead corrosion and control, the use of conditioned new lead test pieces remains a reasonable and representative estimate of worst-case system lead release and response to corrosion control treatment options.

The consistent configuration and operation of any apparatus, whether utilizing conditioned new test pieces or harvested test pieces, creates baseline data against which to compare residential data and uncover discrepancies that can further be investigated. The baseline apparatus data are also compared to trends of other water quality parameters, to empirically look for correlations and hypothesize influential factors in the release of lead and copper. When dominant influential factors are identified, the factors can be manipulated for control of lead or copper release.

The test pieces were also compared by looking at how well results can be reproduced between two new conditioned test pieces and likewise between two harvested test pieces. In terms of reproducibility as displayed in Figure 5, harvested test piece data cannot be distinguished from conditioned new test piece data.

In comparing results from different apparatuses operating in parallel, no two types of apparatuses had consistent comparable results or trends with each other (Figure 6). Figure 6 reflects that variability of results are introduced in apparatuses by differences in test piece ratio of metal surface area to water volume, apparatus operations parameters, and sampling requirements.

There are no scientific reasons to eliminate either type of test piece in lead or copper release testing when keeping in mind the limitations of each method. The observations made in this study suggests that no matter whether test pieces are conditioned new metal or harvested metal, the following criteria should be applied to corrosion control investigations:

- **Maintain consistency of apparatus configuration and operation.** Test pieces in an apparatus should be consistent with each other in the ratio of metal surface area to water volume. Apparatus operations should be consistent in water usage and flowrate throughout a project. The array of scale compounds on test pieces should be similar, or at least, strategically and purposefully different.
- **Determine the properties of distribution system pipe wall accumulations.** Samples of harvested pipe for scale analysis should be analyzed from the distribution system no matter which type of apparatus is used for testing. This will give insight into the potential of lead and copper in pipe wall accumulations in a system to dissolve into the water or to crumble into particulates.
- **Identify metal fractions of the total metal concentrations.** Both dissolved and particulate fractions of lead and copper should be measured and studied. Dissolved lead and copper represent chemical and microbiological corrosion processes. Particulate lead and copper represent entrapment of corrosion by-products by chemical scales and biofilms with erratic release.
- **Place apparatus data in context with residential sampling.** Apparatus data should be compared to residential sampling data as was demonstrated in this research in order to interpret apparatus results.

Accepting the use of conditioned new test pieces for testing and monitoring can lower corrosion control study costs, providing a tool for water systems of all sizes to select the best corrosion control strategy and to pro-actively track lead and copper release trends in the distribution system.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- American Water Works Association (AWWA) 2011 *Manual of Water Supply Practices – M58: Internal Corrosion Control in Water Distribution Systems*, 1st edn. AWWA, Denver, CO, USA.
- American Water Works Association Research Foundation (AWWARF) & DVGW-Technologiezentrum Wasser (DVGW) 1996 *Internal Corrosion of Water Distribution Systems*, 2nd edn. AWWARF, Denver, CO, USA.

- Boyd, G. R., Reiber, S., McFadden, M. S. & Korshin, G. V. 2012 Effect of changing water quality on galvanic coupling. *Journal AWWA* **104** (3), E136–E149. <http://doi.org/10.5942/jawwa.2012.104.0038>.
- Cantor, A. F. 2018 *Water Distribution System Monitoring: A Practical Approach for Evaluating Drinking Water Quality*, 2nd edn. CRC Press, Boca Raton, FL, USA.
- Cantor, A. F., Kiefer, E., Little, K., Jacque, A., Degnan, A., Maynard, J. B., Mast, D. & Cantor, J. 2012 *Project 4286: Distribution System Water Quality Control Demonstration*. Water Research Foundation, Denver, CO, USA.
- Cornwell, D. & Brown, R. 2015 *Project 4569: Evaluation of Lead Sampling Strategies*. Water Research Foundation, Denver, CO, USA.
- Cornwell, D. A. & Wagner, J. A. 2019 Coupon procedures for evaluating lead and copper solubility. *Journal AWWA* **111** (10), 12–24. <http://doi.org/10.1002/awwa.1377>.
- Economic and Engineering Services, Inc. (EES) 1990 *Lead Control Strategies*. AWWARF and AWWA, Denver, CO, USA.
- Fagerbakke, K. M., Heldal, M. & Norland, S. 1996 Content of carbon, nitrogen, oxygen, sulfur and phosphorus in native aquatic and cultured bacteria. *Aquatic Microbial Ecology* **10** (1), 15–27. <http://doi.org/10.3354/ame010015>.
- Gale, W. F. & Totemeier, T. C. 2004 *Smithells Metals Reference Book*, 8th edn. Elsevier Butterworth-Heinemann, Kidlington, Oxford, United Kingdom.
- Harmon, S. M., Tully, J., DeSantis, M. K., Schock, M. R., Triantafyllidou, S. & Lytle, D. A. 2022 A holistic approach to lead pipe scale analysis: Importance, methodology, and limitations. *AWWA Water Science* **4** (2), e1278. <http://doi.org/10.1002/awws.1278>.
- Hazen & Sawyer 2019 *Lead and Copper Corrosion Bench-Scale Testing Guidance Manual*. Colorado Department of Public Health and Environment, Denver, CO, USA. Available from: https://drive.google.com/file/d/1G7N_kbwim1VTnD7gtCNbC8jDRAi7VU_/view.
- Hopwood, J. D., Derrick, G. R., Brown, D. R., Newman, C. D., Haley, J., Kershaw, R. & Collinge, M. 2016 The identification and synthesis of lead apatite minerals formed in lead water pipes. *Journal of Chemistry* **2016**, 9074062. <http://doi.org/10.1155/2016/9074062>.
- Kirmeyer, G. J., Sandvig, A. M., Pierson, G. L. & Neff, C. H. 1994 *Development of A Pipe Loop Protocol for Lead Control*. AWWARF and AWWA, Denver, CO, USA.
- Lagos, G. E., Cuadrado, C. A. & Letelier, M. V. 2001 Aging of copper pipes by drinking water. *Journal AWWA* **93** (11), 94–103. <http://doi.org/10.1002/j.1551-8833.2001.tb09338.x>.
- Liu, S., Gunawan, C., Barraud, N., Rice, S. A., Harry, E. J. & Amal, R. 2016 Understanding, monitoring, and controlling biofilm growth in drinking water distribution systems. *Environmental Science and Technology* **50** (17), 8954–8976. <http://doi.org/10.1021/acs.est.6b00835>.
- Lytle, D. A. & Schock, M. R. 2005 Formation of Pb (IV) oxides in chlorinated water. *Journal AWWA* **97** (11), 102–114. <http://doi.org/10.1002/j.1551-8833.2005.tb07523.x>.
- Parks, J., Edwards, M. & Atassi, A. 2014 *Project 4317: Non-Intrusive Methodology for Assessing Lead and Copper Corrosion*. Water Research Foundation, Denver, CO, USA.
- Reiber, S. 1991 Galvanic stimulation of corrosion on lead-tin solder-sweated joints. *Journal AWWA* **83** (7), 83–91. <http://doi.org/10.1002/j.1551-8833.1991.tb07183.x>.
- Rittmann, B. E. & McCarty, P. L. 2001 *Environmental Biotechnology: Principles and Applications*. McGraw-Hill, New York, NY, USA.
- Schock, M. R., Cantor, A. F., Triantafyllidou, S., Desantis, M. K. & Scheckel, K. G. 2014 Importance of pipe deposits to Lead and Copper Rule compliance. *Journal AWWA* **106** (7), 87–88. <http://doi.org/10.5942/jawwa.2014.106.0064>.
- US Environmental Protection Agency (US EPA). 2021 National primary drinking water regulations: Lead and Copper Rule revisions. *Federal Register* **86**, 4198–4312.
- Wheeler, D. J. & Chambers, D. S. 1992 *Understanding Statistical Process Control*, 2nd edn. SPC Press, Knoxville, TN, USA.
- Williams, D. J., Parrett, C. J., Schock, M. R., Muhlen, C., Donnelly, P. & Lytle, D. A. 2018 Design and testing of USEPA's Flint pipe rig for corrosion control evaluation. *Journal AWWA* **110** (10), E16–E37. <http://dx.doi.org/10.1002/awwa.1127>.
- Wysock, B. M., Sandvig, A. M., Schock, M. R. & Frebis, C. P. 1995 Statistical procedures for corrosion studies. *Journal AWWA* **87** (7), 99–112. <http://doi.org/10.1002/j.1551-8833.1995.tb06397.x>.

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