CORNWELL
ENGINEERING GROUP

June 23, 2022

Benton Harbor – Corrosion Optimization
Engineering Memorandum No. 16100-01
Subject: Lead Solubility Study Summary

OVERVIEW

Cornwell Engineering Group (Cornwell) has been tasked to evaluate corrosion control treatment (CCT) for the City of Benton Harbor (the "City") and the State of Michigan Department of Environment, Great Lakes, and Energy (EGLE). Currently, the target CCT of the City was set by EGLE as 3 mg/L as PO_4 for the orthophosphate fraction of a 90/10 blended phosphate beginning February 2020. However, this target was determined using the "analogous systems" approach (USEPA 2016, p. F-1[1]), and therefore a system-specific study was conducted in this project to compare selected CCT approaches.

The source water for the Benton Harbor Water Treatment Plant (WTP) is Lake Michigan, and treatment includes conventional processes (coagulation, flocculation, clarification, filtration) using the following treatment chemicals: alum, sodium hypochlorite, sodium fluoride, and a 90/10 blended phosphate product (90% sodium orthophosphate (NaH_2PO_4) and 10% polyphosphate). The finished water has a typical pH of 8.0 to 8.2, alkalinity 115 mg/L as $CaCO_3$, calcium hardness about 43 mg/L (108 mg/L as $CaCO_3$), chloride 24 mg/L, and sulfate 33 mg/L. The resulting calculated characteristics of the finished water are as follows:

- Dissolved inorganic carbon (DIC) of 28 mg/L as C,
- Saturation pH ($CaCO_3$) of 7.9 and the resulting Langelier Saturation Index (LSI) +0.3
- Calcium carbonate precipitation potential (CCPP) of +4.4 mg/L as $CaCO_3$,
- Larson-Skold Index (LSK) of 0.6 meq/meq,
    - The LSK is used to describe the corrosivity of water towards iron, although it does not account for all iron corrosion mechanisms. An LSK <0.8 meq/meq suggests that the water quality conditions are not conducive to iron corrosion
- Chloride to sulfate mass ratio (CSMR) of 0.7 mg/mg.
    - Nguyen et al. (2013) report CSMR ≤0.5 mg/mg are not susceptible to galvanic corrosion. The 0.7 mg/mg CSMR is above this recommended target but the general concern is a changing CSMR and this CSMR has been steady and not expected to increase.

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[1] USEPA 2016. Optimal Corrosion Control Treatment Evaluation Technical Recommendations for Primacy Agencies and Public Water Systems (EPA816-B-16-003). USEPA-Office of Water: Washington, DC.

There is currently no pH adjustment at Benton Harbor, and since NaH_2PO_4 in the blended phosphate will not change pH much (lowering pH ≤0.1), the finished water pH typically remains about 8.2. The current CCT includes addition of the 90/10 blended phosphate product to achieve a target residual of 3.0 mg/L as PO_4 for the orthophosphate fraction (3.3 mg/L as PO_4 or 1.1 mg/L as P for total phosphate). In this memorandum, the following terms will be used for phosphate doses and residuals: "o-PO_4"= orthophosphate, "t-PO_4"= total phosphate, and "p-PO_4"= polyphosphate.

LEAD SOLUBILITY TESTING

The City's current 90/10 product was tested using varying doses and pHs. In addition, the blended phosphate was compared to a straight orthophosphate. During the solubility testing with new lead coupons, the current 90/10 blended phosphate product was dosed at 2, 3, and 4 mg/L as o-PO_4 with pH adjusted to the current 8.2. These results were compared to identical doses at pH 7.8 (the optimal pH for lead solubility control with orthophosphate is typically 7.2 to 7.8). The actual pH for the pH 7.8 testing was about 7.6, but it generally referred to as 7.8 in the graphs. The above test conditions with the 90/10 product were compared to similar 2, 3, and 4 mg/L as o-PO_4 doses of phosphoric acid (H_3PO_4). The H_3PO_4 were tested under "pH float" conditions, meaning the pH was adjusted to 8.2 and then H_3PO_4 added, producing lower pH as the o-PO_4 dose increased (see later pH data). Additionally, to evaluate the potential impacts of the test conditions on chrome faucets and brass fittings, new brass coupons were tested at a target dose of 3 mg/L as o-PO_4 at the same pH conditions as the lead coupons for both the 90/10 and H_3PO_4 products. The study began December of 2021 and ended April of 2022. In March 2022, upon discovering the pH of the City's distribution system were averaging at slightly higher pH values, all 8.2 pH conditions using the 90/10 blended phosphate were changed to pH 8.5. Table 1 shows all the CCT parameters tested, creating a total of 16 conditions.

Table 1
Conditions Tested.

Orthophosphate Product	90/10 Blend		H_3PO_4	
Test Material	Lead	Brass	Lead	Brass
Orthophosphate Dose (mg/L as o-PO_4) †	2, 3, 4	3	2, 3, 4	3
Target pH	7.8, 8.2, 8.5		‡	

† For the blended phosphate, this is the dose of the orthophosphate fraction

‡ The pH was adjusted to 8.2 (current finished water pH), and then H_3PO_4 added. This condition is called a "pH float" in this study since the final pH is not adjusted after H_3PO_4 addition.

PROCEDURES

Coupon Assembly

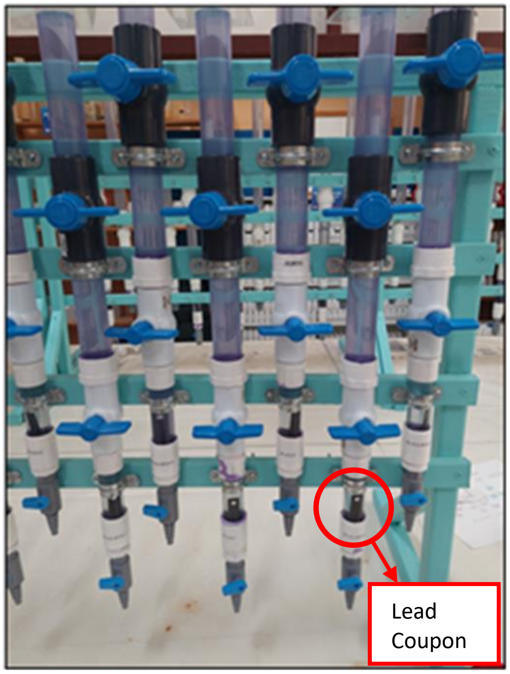

Figure 1 Example Test Assemblies

New lead or brass coupons were suspended inside a 60-mL PVC pipe chamber. Two ball valves were connected to both ends to produce headspace-free pH conditions. Two additional 60-mL PVC chambers were stacked above the coupon chamber to maintain a submerged coupon during collection of water samples. Figure 1 shows an example setup of the test assemblies.

Coupons

The lead coupons are essentially 100 percent lead. The brass coupons used for the study were the UNS# C84400 alloy ("semi-red brass"), which contains 6 - 8% lead and 7 - 10% zinc. All lead and brass coupons were new and unopened from their sealed plastic bags.

Water Preparation

Water from Benton Harbor Water Works was shipped in 5-gallon plastic buckets to Newport News, VA for testing. Prior to water preparation, which occurred every Tuesday and Thursday, water was collected from the buckets, chemically adjusted, and then distributed to each assembly so that all assemblies were filled with water. The top chamber was capped with a plexiglass plate sealed from the atmosphere. Each weekday all valves were opened to allow water to flow out of the chamber with the lead and replaced with water from the chamber above. In this way the lead coupon was not disturbed by transferring it to a new chamber or jar and was always exposed to water. After flowing the water all valves are closed again. Sampling for lead analysis occurred the day after water preparation, every Wednesday and Friday after siting stagnant overnight. The stagnation time was generally about 20 hours (2 pm to 10 am).

Chemical adjustment included the addition of a target dose of phosphate (orthophosphate or 90/10 polyphosphate blend depending on the treatment conditions), chlorine from NaOCl stock solution (strength of solution checked daily, resulting residual verified, and dose adjusted as needed). The pH was adjusted by an automatic titrator with H_2SO_4 or NaOH as needed.

The day after water preparation, 60-mL samples were collected for lead analysis. All lead samples were acidified for at least 24 hours prior to analysis.

Chlorine Adjustment

Water was dosed to achieve a 1.8 mg/L as Cl_2 free chlorine residual. Chlorine dosing was performed with sodium hypochlorite (NaOCl) stock solution and tested with a Hach DR4000U spectrophotometer. The NaOCl solution was prepared freshly each day of water preparation using a 1:50 dilution of sodium hypochlorite solution.

Phosphate

The 90/10 phosphate blend was dosed using a 1:250 dilution of Aquadene SK-7661 (Carus Corp., Peru, IL). SK-7661 is a blended phosphoric acid product containing 27.8% by weight of orthophosphate as o-PO_4 and 3.8% by weight of polyphosphate as p-PO_4. H_3PO_4 was dosed with a 1:250 dilution of SLI-PHOS-36 (Shannon Chemical Corp., Malvern, PA), a product containing 36% by weight of orthophosphate as o-PO_4. Dosing took place prior to pH adjustment for conditions treated with SK-7661, and after pH adjustment for those given SLI-PHOS-36. Dosing conditions are noted in Table 1.

pH Adjustment

A Hannah Instruments HI-902 automatic titrator was used for pH adjustment using 0.1 N NaOH and/or 1 N H_2SO_4 solution as needed to achieve the target pH after all other chemicals described earlier were added. Beginning March 2022, all 8.2 pH conditions not dosed with H_3PO_4 were changed to an 8.5 target pH.

RESULTS

Bench-scale solubility studies are useful at showing relative comparisons of different test conditions. In this study, the impact of different products, target pH, and target o-PO_4 dose were compared[2]. However, the results are not predictive of final lead concentrations in compliance or other household lead samples in the system. Therefore, the data in following graphs (and associated statistical analyses) can indicate which pH, dose, or product produces lower or higher lead than some other treatment combination tested, but these results will not predict the actual numerical value of the lead concentrations that will occur within the Benton Harbor distribution system. These tests also do not predict scale impacts on lead release. In this case, the City already uses orthophosphate so the tests are very useful in comparing doses and phosphate type.

Water sampling began in December 2021 and ended in April 2022. The study ended when all conditions became stable with enough equilibrated samples for statistical analysis.

All statistical tests were conducted at a 95% confidence interval. Comparisons were made between steady state results. For example, Figure 2 shows all the data for one test condition (shown with an "X"), and the data used to determine steady state conditions (shown with a blue square). The graph was used to visually evaluate dates where lead solubility was leveling, and

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then attainment of steady state (i.e., stable lead results) was statically confirmed using Spearman or Pearson's correlation, and 95 percent confidence intervals. The stable or "equilibrium" data (i.e., squares in Figure 2) were evaluated and compared to other test conditions using Mann-Whitney U tests.

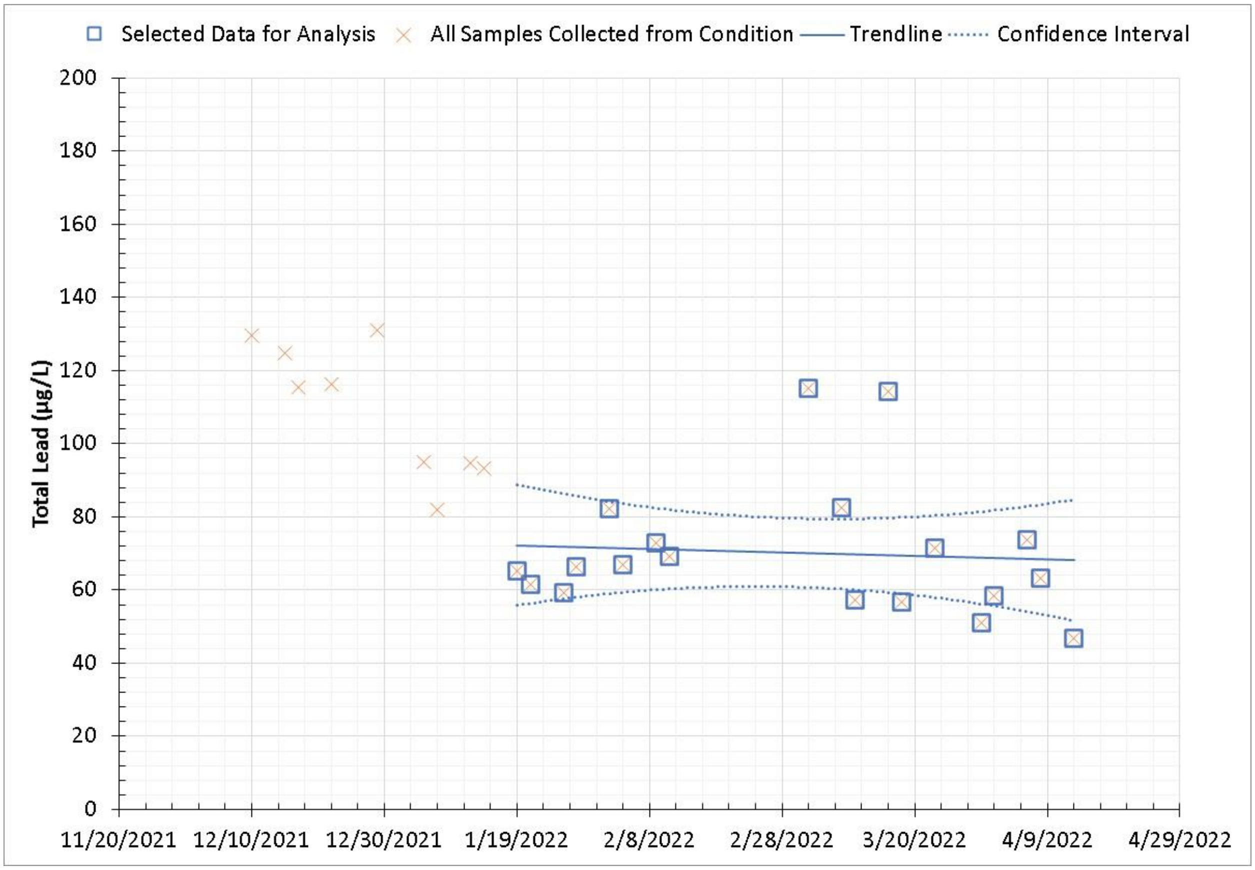


Figure 2 **Example time series showing all data ("X") and equilibrated data used for statistical comparison to other test conditions**

Note: This example is for a lead coupon, H_3PO_4, pH float, 2 mg/L as o-PO_4

The observations based on these data are discussed below.

Impact of pH on lead solubility in the presence of orthophosphate

Increasing the pH generally decreased lead levels, as shown in Figure 3. In addition, Figure 4, Figure 5, and Figure 6 show the same data, but in more detail, with each graph showing data for each o-PO_4 dose.

- For the 90/10 product, the 8.5 pH conditions showed the lowest lead levels compared to the 8.2 pH and 7.8 pH conditions, and the 8.2 pH conditions showed lower lead levels than the 7.8 pH conditions.
- The results with H_3PO_4 (pH float) were not statistically different from the 8.2 pH conditions for 90/10 blend at lower doses (2 and 3 mg/L as o-PO_4), but lead results with H_3PO_4 were higher than the 90/10 product at a 4 mg/L dose. The median pH of the H_3PO_4 dosed water was ~7.85 at the 4 mg/L as o-PO_4 dose, 7.93 at 3 mg/L as o-PO_4, and 8.00 at 2 mg/L as o-PO_4.
- The differences and similarities noted above for lead results were statistically significant, based on statistical approaches and assumptions (i.e., 95% confidence interval) noted in this memorandum.

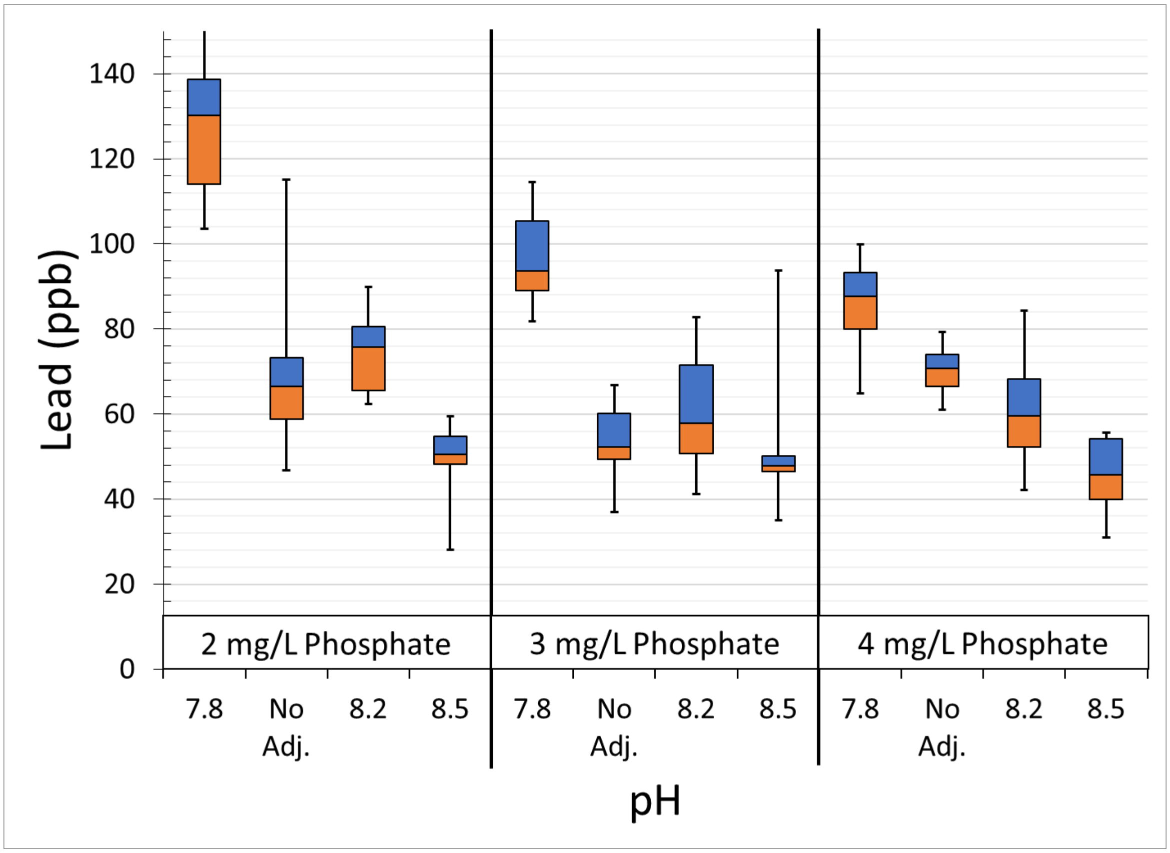
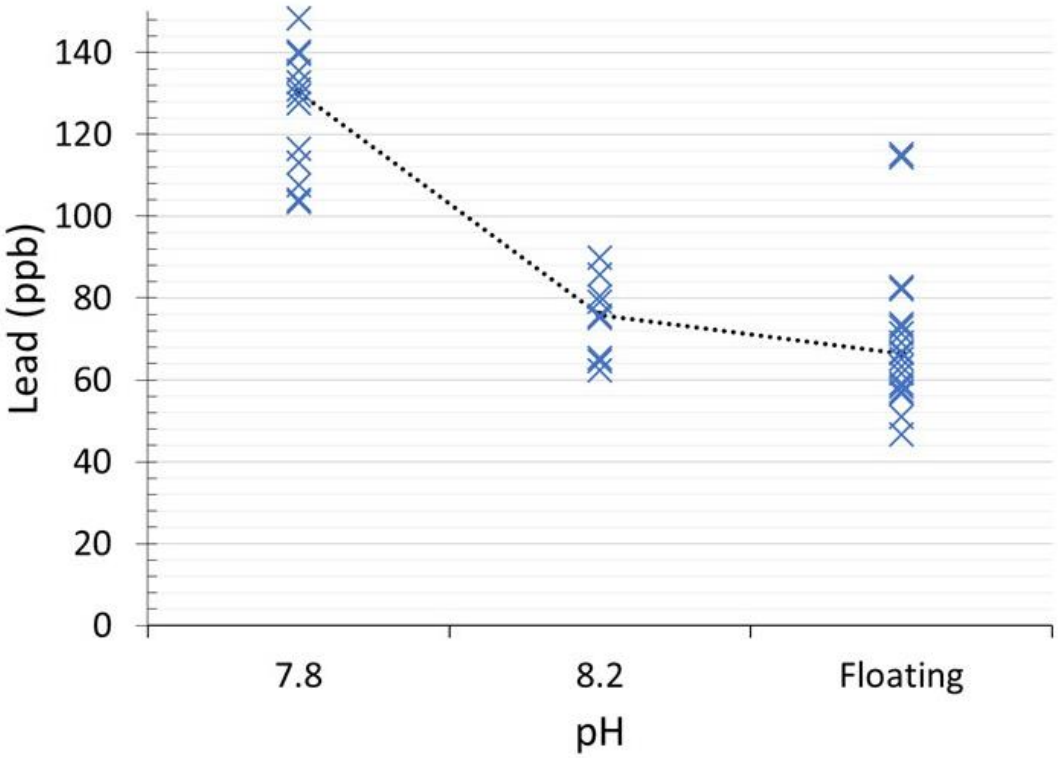
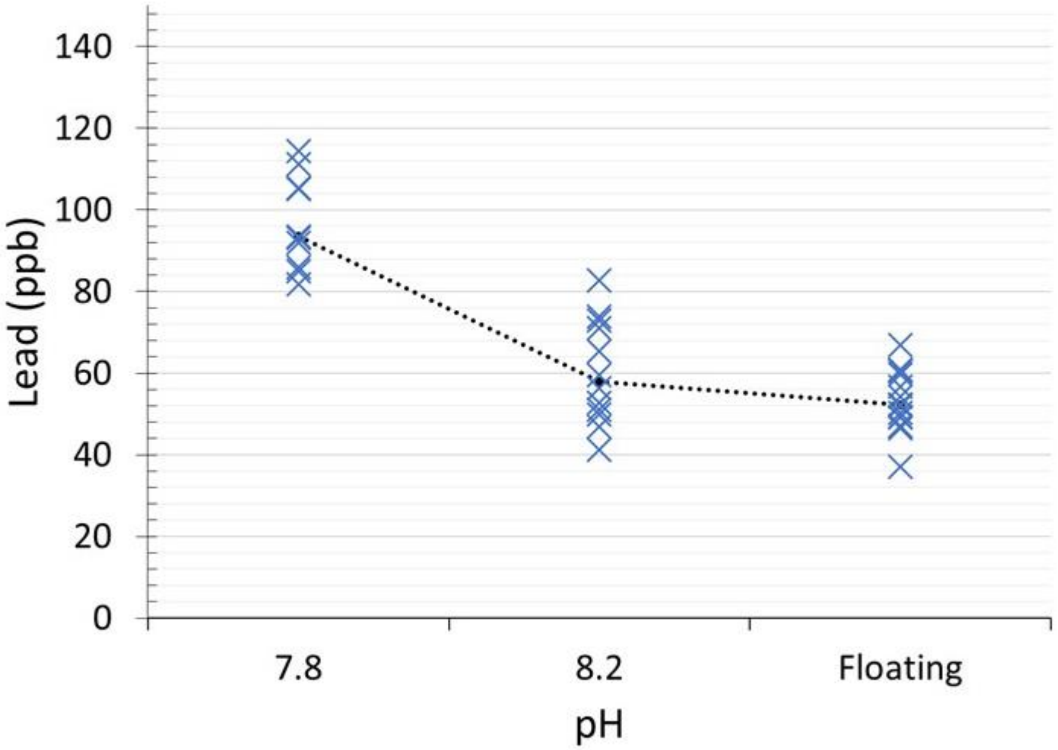


Figure 3 **Comparison of lead for 2, 3, and 4 mg/L o-PO_4 dose. The "No Adj." is H_3PO_4, while the remainder are the 90/10 blend.**



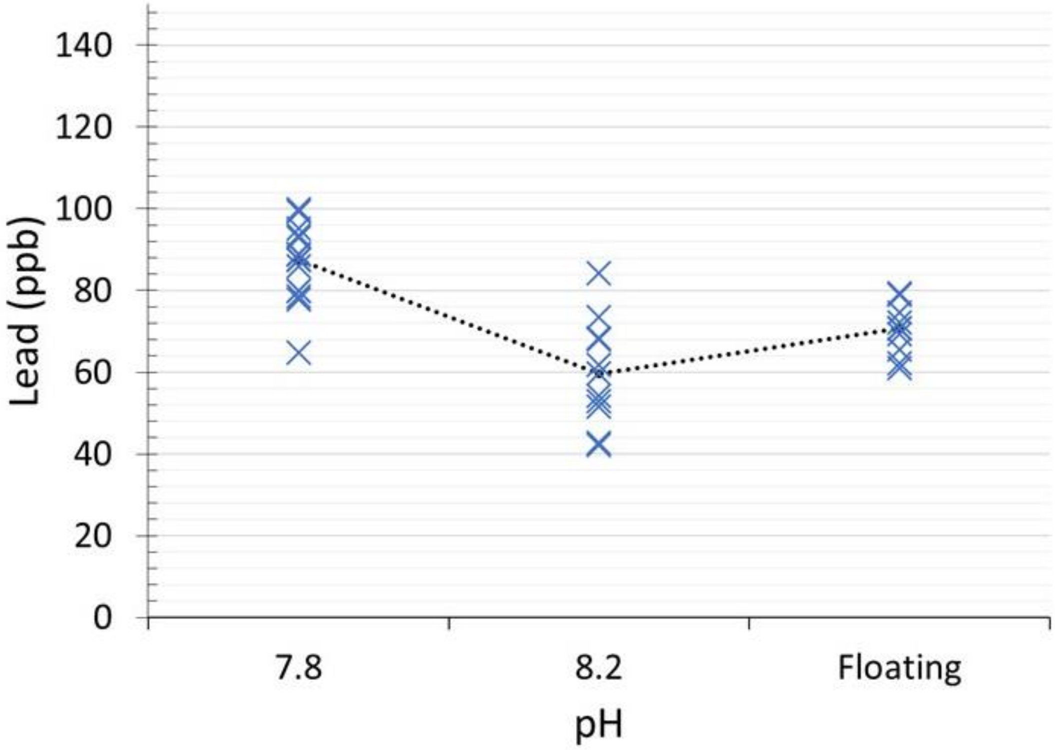
Statistical Rank	**3rd**	**Tied for 1st**	**Tied for 1st**

Figure 4 **Lead Coupons with 2 mg/L o-PO_4.**



Statistical Rank	**3rd**	**Tied for 1st**	**Tied for 1st**

Figure 5 **Lead Coupons with 3 mg/L o-PO_4.**



Statistical Rank	**3rd**	**1st**	**2nd**

Figure 6 Lead Coupons with 4 mg/L o-PO_4.

Impact of orthophosphate dose on lead solubility

Lead decreased at higher doses for H_3PO_4 and the 90/10 blend product, as seen in Figure 7, under most conditions tested. Figure 8, Figure 9, and Figure 10 show the same data in greater detail for the 90/10 blend product at different pH, while Figure 11 shows the pH float data for H_3PO_4.

- For the 90/10 blend product, the decreased lead at higher doses is especially noticeable at the 7.8 pH conditions. At pH 8.2, there is not a statistically significant difference in the 3 and 4 mg/L as o-PO_4 results, but the difference between both is statistically significant compared to the lead results at the 2 mg/L as o-PO_4 dose. At pH 8.5 there was no statistical difference in lead levels at the three doses of the 90/10 blend product tested.
- Lead results with H_3PO_4 were lowest at 3 mg/L as o-PO_4. It is not particularly logical that the 4 mg/L dose was higher and is likely an anomaly.

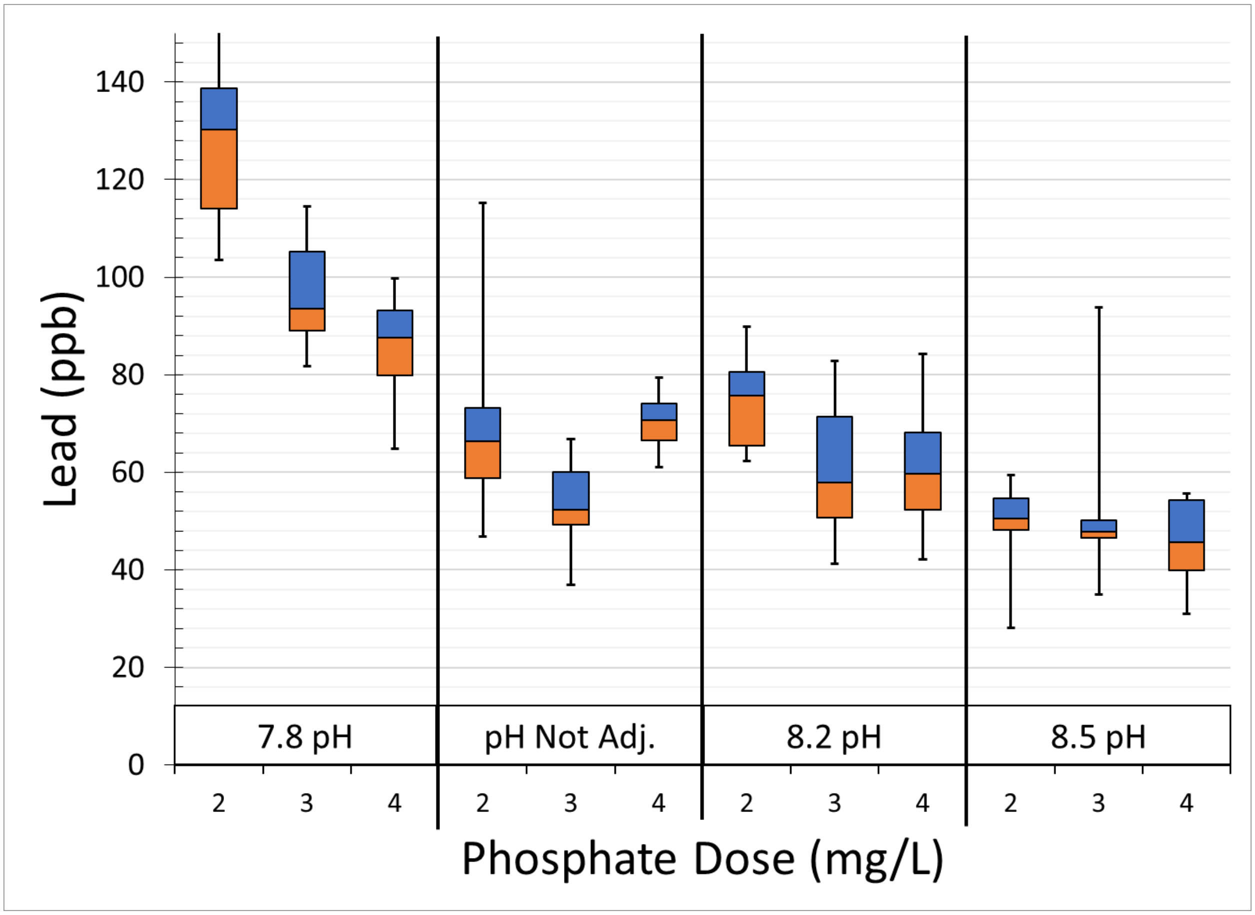
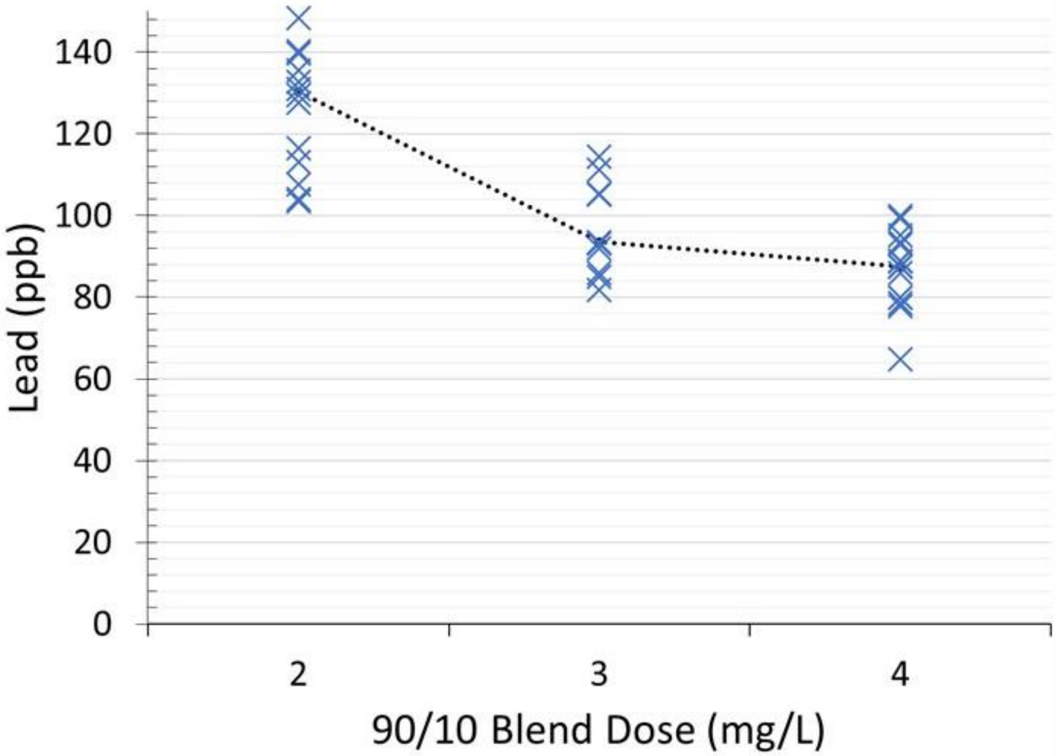
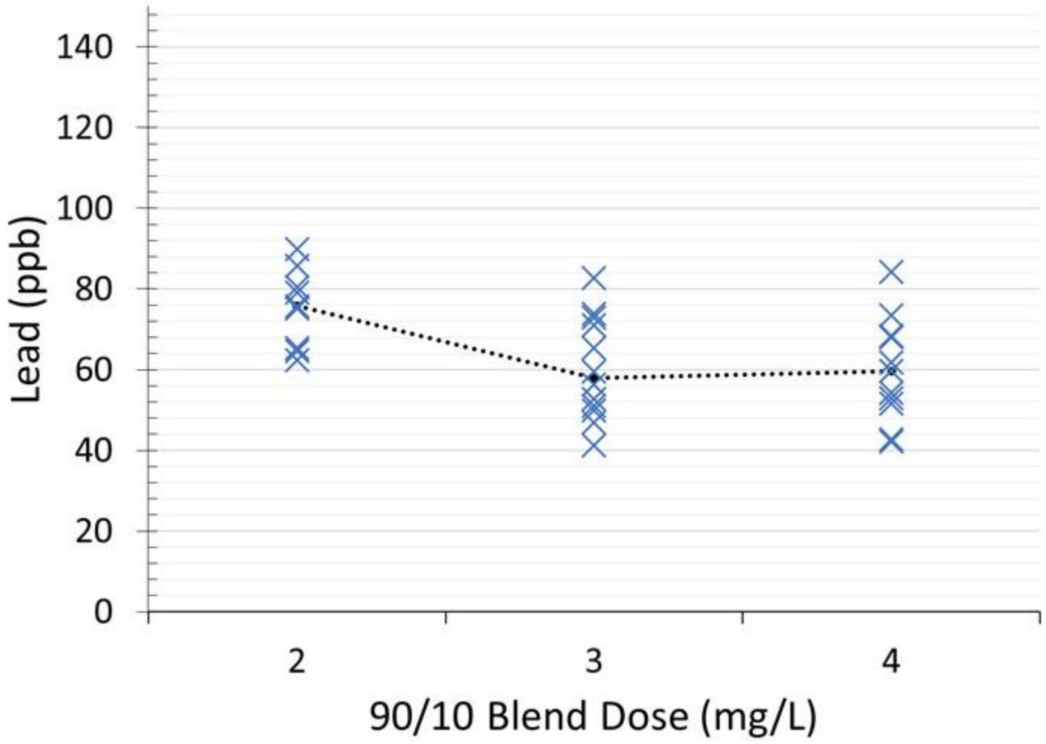


Figure 7 **Phosphate dose comparisons at 7.8 pH, 8.2 pH, 8.5 pH, and the orthophosphate treatments (pH was not adjusted, but averaged around 7.9).**



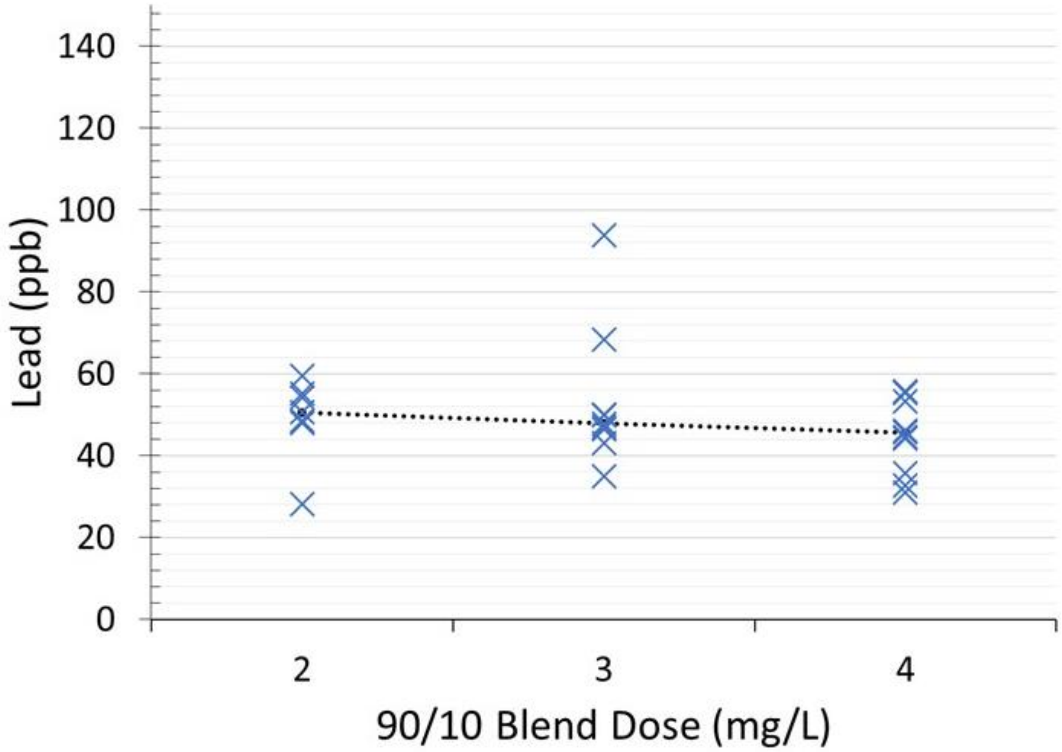
Statistical Rank	**3rd**	**2nd**	**1st**

Figure 8 Lead Coupons, 90/10 blend, pH 7.8, with 2, 3, and 4 mg/L o-PO$_4$.



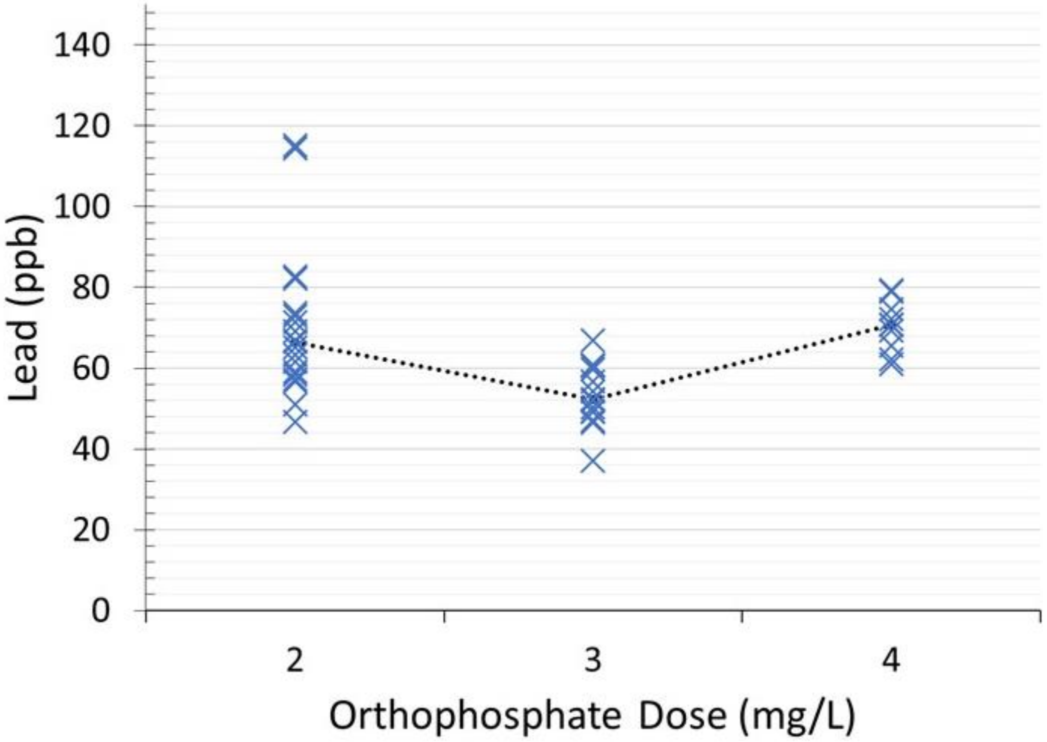
Statistical Rank	**3rd**	**Tied for 1st**	**Tied for1st**

Figure 9 Lead Coupons, 90/10 blend, pH 8.2, with 2, 3, and 4 mg/L o-PO$_4$.



Statistical Rank	**Tied for 1st**	**Tied for 1st**	**Tied for 1st**

Figure 10 **Lead Coupons, 90/10 blend, pH 8.5, with 2, 3, and 4 mg/L o-PO_4.**



Statistical Rank	**Tied for 2nd**	**1st**	**Tied for 2nd**

Figure 11 **Lead Coupons, H_3PO_4, pH float, with 2, 3, and 4 mg/L o-PO_4.**

Comparison of lead solubility for treated water in contact with brass versus lead

Brass coupons showed statistically lower levels than lead coupons at 7.8 pH. For all other pH conditions tested, brass and lead coupons showed no statistical difference. There was no statistically significant difference between any of the pH values tested with brass coupons using either product under the conditions tested (3 mg/L as o-PO_4), except between the 8.2 and 8.5 pH results (lead at 8.2 pH is lower than 8.5 pH, and the difference is statistically significant). Comparisons between the lead and brass coupons are shown in Figure 12.

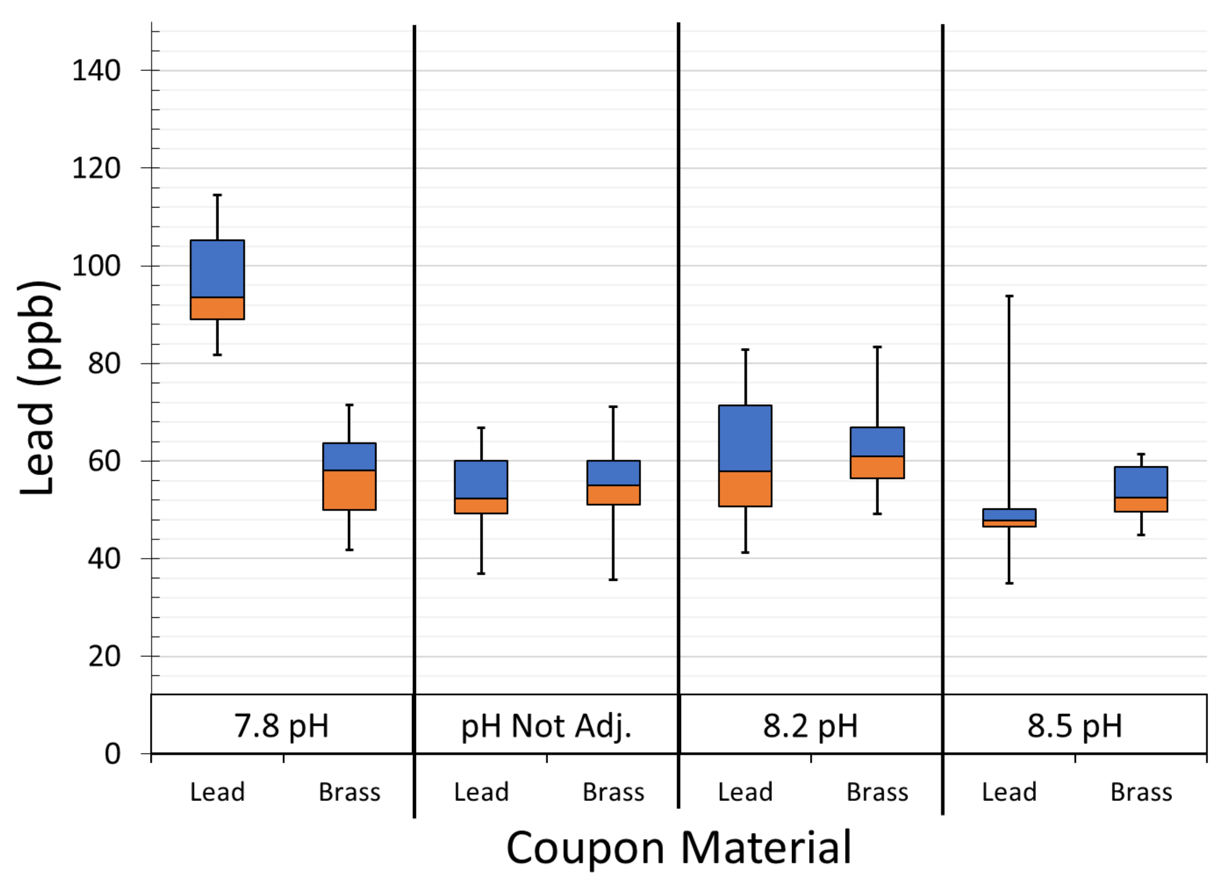


Figure 12 **Coupon material comparisons at 7.8 pH, 8.2 pH, 8.5 pH, and the orthophosphate treatments (pH was not adjusted, but averaged around 7.9).**

Discussion of Findings

The results imply that a higher pH was more effective at reducing lead and the dose of orthophosphate (90/10) did not matter at the higher pH tested. However, further analysis revealed that that is not necessarily the case. Orthophosphate is typically more effective at limiting lead solubility at pH <8, contrary to these findings. Lead solubility at pH 8.5 can be controlled by solubility of lead carbonate scale, particularly the formation hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) at pH >7.5, as shown in Figure 13. Because there was concern that the test results seemed to indicate that the higher pH with orthophosphate performed the best, lead solubility was analyzed relative to lead carbonate species. Theoretical lead solubility was modeled using Visual MINTEQ v. 3.1 software as shown in Figure 13. These modelled results use the DIC shown earlier (28 mg/L). For the infinite cerussite (black dashed line) and infinite hydrocerussite models (solid red line), no orthophosphate is assumed to be present. The red "X" indicates the point where cerussite and hydrocerussite solubility are similar, with cerussite solubility lower than hydrocerussite solubility at lower pH and hydrocerussite solubility lower than cerussite at higher pH. The infinite hydroxylpyromorphite model, shown as a dashed blue line, assumes 3 mg/L o-PO_4 present. The modeled results do not take into account the impact of polyphosphate or the presence of lead in +4 oxidation state (Pb(IV)).

This figure indicates that, without o-PO_4, the lead decreases with increasing pH from 7.8 to 8.8, as was shown in the coupon study results. Theoretically, this curve indicates that in the presence of 3 mg/L o-PO_4, the lead(II) solubility would be lowest at pH values between 7.5 and 8.0.

Figure 15 compares the theoretical lead carbonate solubility relationship at DIC 30 mg/L (similar to the 28 mg/L DIC at Benton Harbor) with experimental lead solubility data from a research project Cornwell is conducting. The Cornwell experimental study results indicate that the actual lead solubility is higher than predicted by the MINTEQ program using these experimental data at 30 mg/L DIC. The lead solubilities at different pH were estimated as shown in orange and as highlighted in text with arrows. These data were used to estimate a corrected solubility curve for lead carbonate in Figure 15, with data points indicated for results at 3 mg/L o-PO_4 using the 90/10 blend (orange "X") and H_3PO_4 (blue square) during the Benton Harbor study. The lead results with the 90/10 blend product closely follow the corrected lead solubility curve assuming control by lead carbonate, indicating that phosphate is not contributing any additional lead solubility control. On the other hand, the H_3PO_4 results are much lower than the lead carbonate curve, suggesting the lead phosphate scale formed under these conditions did lower lead solubility.

What is believed to be occurring in the coupons is that, at the higher pHs of 8.2 and 8.5, lead was controlled by the solubility of lead carbonates and the o-PO_4 probably had little influence on the lead results. Recalling Figure 7, at pH 8.5 all orthophosphate doses had the same lead result, confirming that the o-PO_4 had little or no effect on lead and the lower lead was likely a result of lower lead solubility of lead carbonate species at this pH. Similarly, at pH 8.2 the o-PO4 seemed to have little effect in lowering lead. Figure 14 and Figure 15 can be used to further explore the possibility that lead carbonates were controlling lead at pH 8.2 and 8.5. Figure 14 shows controlled lead results for coupon data developed by Cornwell Research Group. For a DIC of 30 mg/L C, the data matches the theoretical curve quite well but are slightly above the curve. Figure 15 is a curve fit for the coupon data from Figure 14, referred to as the experimental curve. This is what we would expect to see if the lead solubility were controlled by lead carbonates. The test results at pH 8.5 fall right on the line for lead carbonates. This confirms the phosphate was not affecting lead solubility at this pH. On the other hand, both the 90/10 product at pH 7.8 and the phosphoric acid float showed significant improvement using phosphate over simple lead carbonate solubility.

The dose levels and resulting lead at pH 7.8-7.6 seem the most representative of phosphate impacts. If so, we need to look to the pH 7.6/7.8 results with 90/10 blend or H_3PO_4 results (~7.9 pH) to see dose effects of o-PO_4. Therefore, the impact of adding o-PO_4 is strictly observed from the results from the 90/10 blend at pH 7.8 (Figure 8) and H_3PO_4 at float pH 7.9 to 8.0 (Figure 11).

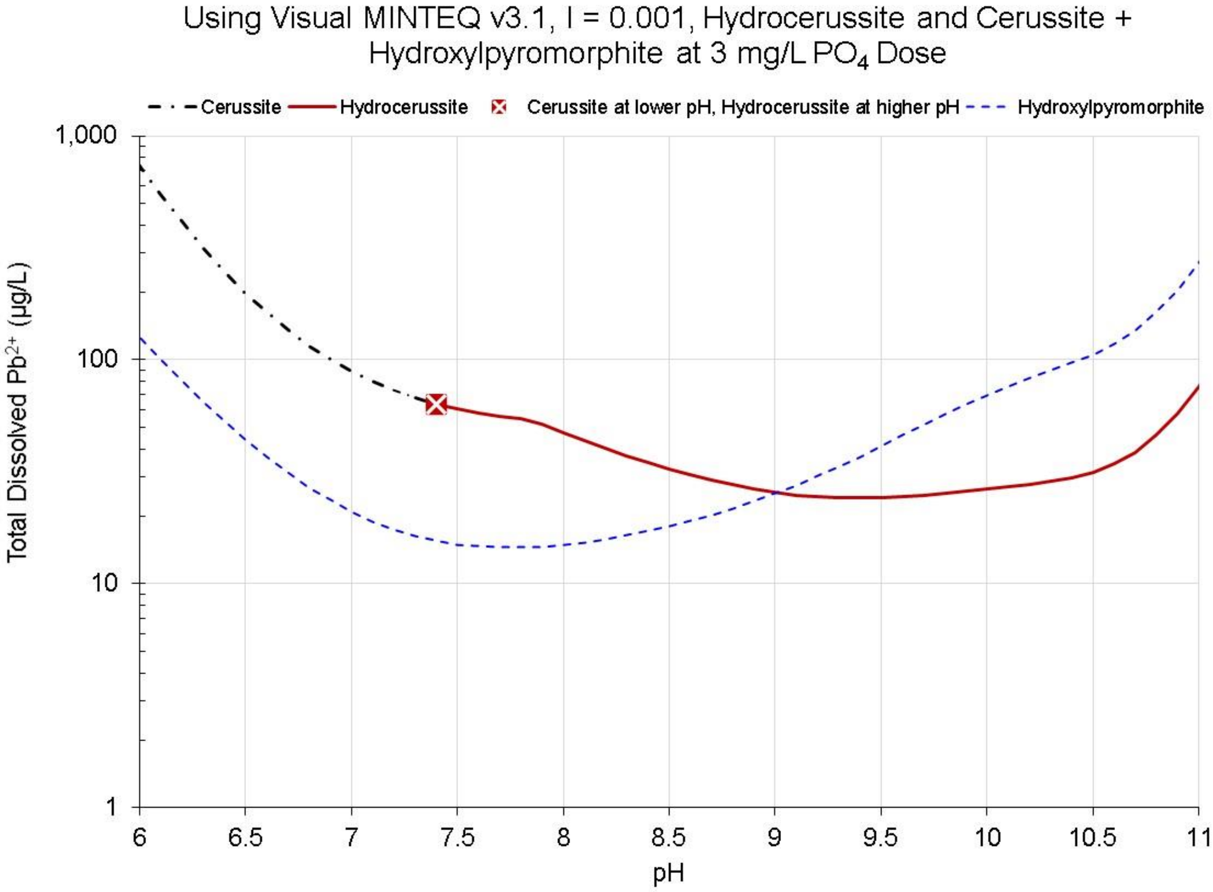


Figure 13 Theoretical solubility of lead (II) in Benton Harbor finished water: a) with orthophosphate present (hydroxylpyromorphite curves) and b) without orthophosphate (hydrocerussite/cerussite curves)

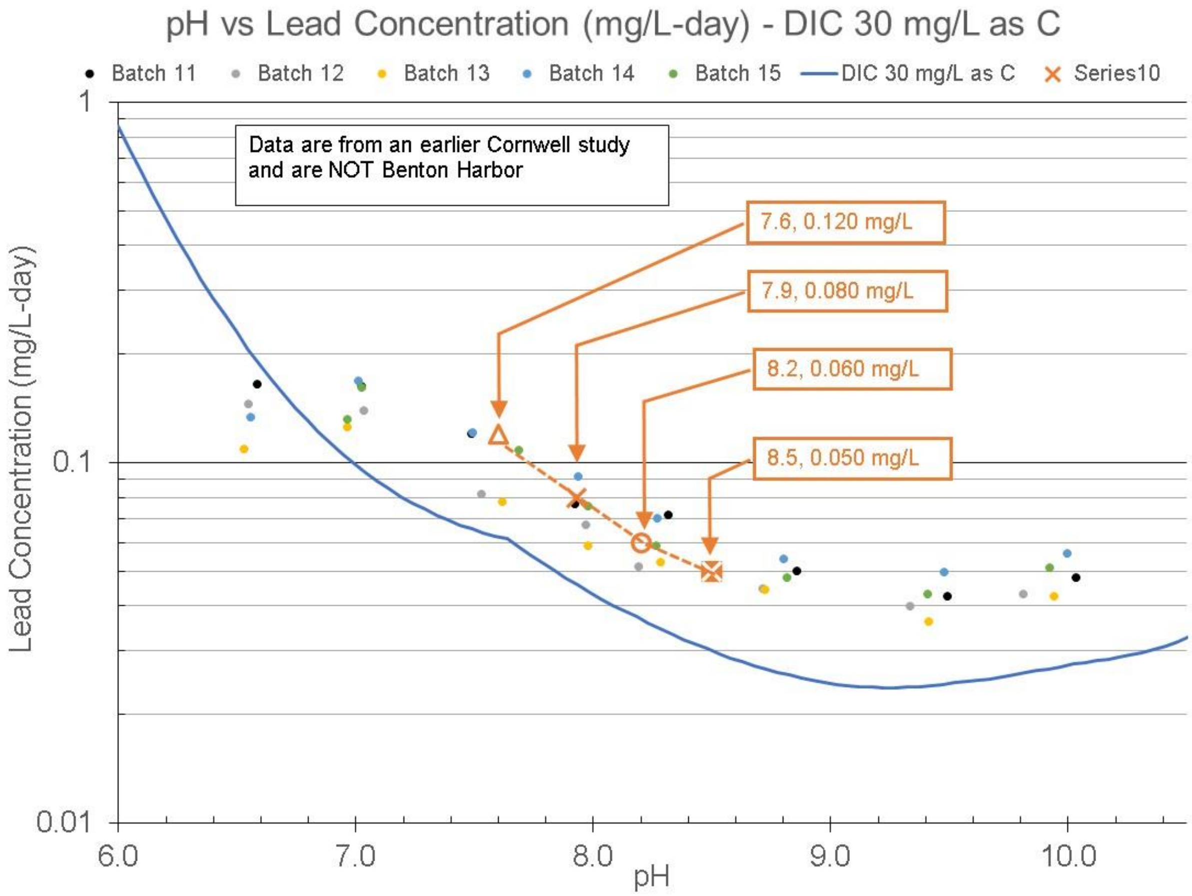


Figure 14 **Cornwell unpublished experimental lead (II) solubility (data points) study data compared to modeled solubility at 30 mg/L DIC as a function of pH**

Note: Experimental results (these are from a previous study and are not from Benton Harbor) indicate that lead (II) carbonates have slightly higher solubility than modeled solubility using VisualMINTEQ. At 8.5 pH the experimental results are about 0.050 mg/L (50 µg/L), 0.060 mg/L at 8.2 pH, 0.120 mg/L at 7.6 pH, and 0.080 mg/L at pH ~7.9 for 3 mg/L o-PO_4 using H_3PO_4.

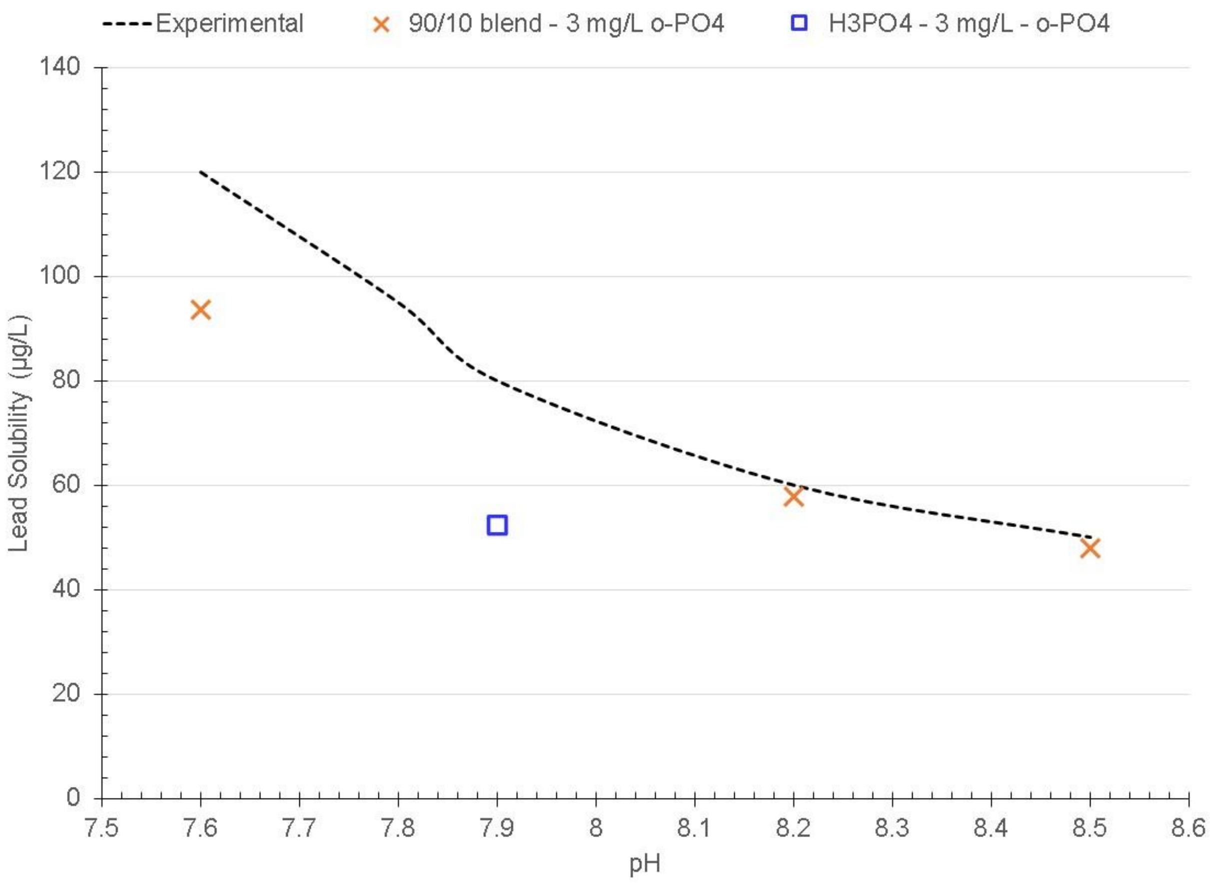


Figure 15 Experimental (Figure 14) lead carbonate species solubility compared to Benton Harbor bench solubility results at 3 mg/L o-PO_4

DISCUSSION OF THE IMPLICATIONS OF BENCH SOLUBILITY TEST RESULTS

The current target CCT of the City's distribution system incorporates a 90/10 blend of polyphosphate dosed at 3 mg/L as o-PO_4. Historical pH and phosphate WQP sample data provided to Cornwell, shown in Figure 16, indicate that the City's distribution system had phosphate between 3 mg/L and 4 mg/L since mid-2021 but was not achieving those targets previously.

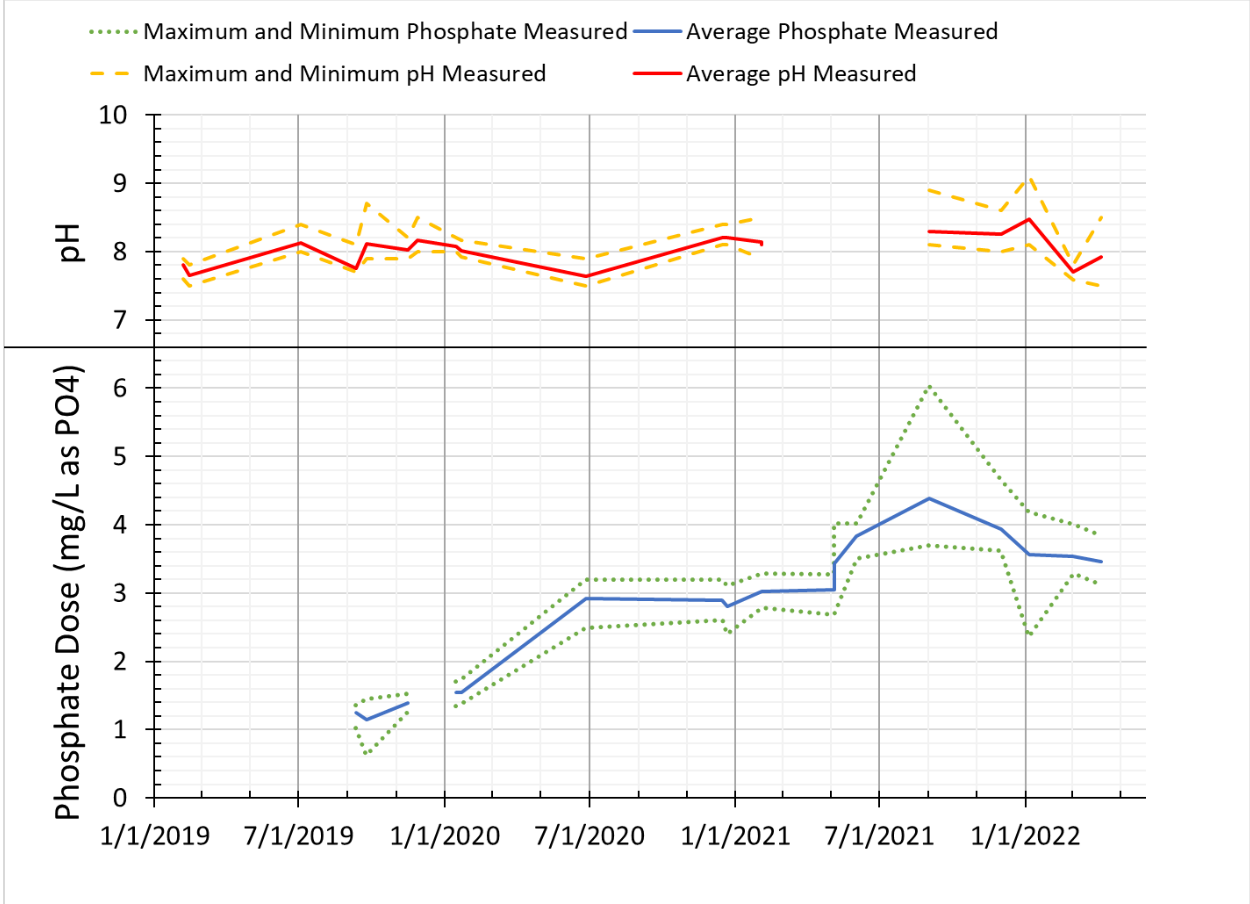


Figure 16 Historic pH and phosphate levels available to Cornwell.

Two issues seem apparent. First, the o-PO4 has not been consistently above 3 mg/L until mid-2021 and has recent minimums below 3 mg/L. Second, the pH in the distribution is generally over 8, and often 8.2 to 8.5. Testing showed with the 90/10 product indicated that the dose needs to be at 3 to 4 mg/L and pH 8 or below for the orthophosphate to be most effective.

RECOMMENDATIONS

- When the 90/10 blended phosphate product is used, adjust the dose to achieve a 3 to 4 mg/L o-PO_4 residual throughout the distribution system. We recommend a dose of 3.8 mg/L o-PO_4 and that the target be achieved at ±0.2 mg/L. The levels in the distribution system should be monitored to always have a residual above 3.0 mg/L and preferably around 3.5 mg/L.
- The distribution system pH needs to be investigated and causes for the higher pH determined and corrected if possible. Causes and methods to decrease the pH could include:
  - Increasing alum dose
  - Using an acid alum product
  - Adding acid post treatment—although we suspect the pH should actually be lower in coagulation to optimize TOC removal and lower aluminum residuals
  - Reducing water age if it is found this is an issue

It is not a good idea at this time to alter coagulant types or doses to achieve a lower pH. Changes should be avoided while lead is still stabilizing and appears to be dropping but testing at lab scale could begin for possible implementation later. However, any methods now to lower the pH, short of a coagulant or similar change, would be beneficial and should be implemented.

- Converting from a blended phosphate to a product containing only orthophosphate (e.g., H_3PO_4) could lower the pH and has the potential to lower lead further than the 90/10 — see Figure 15. Again, we do not suggest a change now as lead is stabilizing, but the City might work toward a switch in the future.
- While this short-term testing found no benefit from orthophosphate at the higher pHs, with time some lead phosphates should develop and help lower lead; however, lowering pH would still be more effective at reducing lead. The City seems to be seeing some improvements in compliance lead samples as the target dose is now being achieved.