APPENDIX E

LEAD CORROSION CONTROL TREATMENT COUPON STUDY TECHNICAL MEMORANDUM

CORNWELL
ENGINEERING GROUP

Date: November 20, 2017

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Project: City of Flint, MI
Water Distribution System Optimization Plan

Subject: Lead Corrosion Control Treatment Coupon Study

OVERVIEW AND TEST CONDITIONS

This corrosion coupon study analyzed water from the City of Flint Water Service Center. The bench-scale coupon immersion test was performed in order to assess the relative solubility of lead under various corrosion control treatment (CCT) scenarios. Testing was performed for 12 weeks.

Table 1 shows the test conditions for this study. Six different orthophosphate dosages were tested at two different target pH levels. In addition to orthophosphate addition and pH adjustment, all water, regardless of test conditions, was disinfected with sodium hypochlorite in order to achieve a free chlorine target concentration of 1.0 mg/L. Each test was completed in duplicate such that two coupons were subjected to each test condition.

Table 1
Study test matrix

Number of Conditions Tested			
Target pH	Orthophosphate (mg/L as PO_4)	Target Free Chlorine (mg/L)	Replicates
7.2	2.0	1	2
	2.5	1	2
	3.0	1	2
	3.5	1	2
	4.0	1	2
	5.0	1	2
7.5	2.0	1	2
	2.5	1	2
	3.0	1	2
	3.5	1	2
	4.0	1	2
	5.0	1	2
	Total Number of Samples		***24***

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Twenty-four coupon apparatuses were assembled with a single lead coupon each. Coupons were assigned to a single water condition noted by a sample identification code (ID). These sample IDs were used throughout this memorandum and in figures displaying results. For reference, Figure 1 provides a Sample ID Legend.

1. ***SOURCE WATER*** • **F** – City of Flint water	2. ***CORROSION INHIBITOR DOSE*** • **2.0 –** 2.0 mg/L as PO_4 • **2.5 –** 2.5 mg/L as PO_4 • **3.0 –** 3.0 mg/L as PO_4 • **3.5 –** 3.5 mg/L as PO_4 • **4.0 –** 4.0 mg/L as PO_4 • **5.0 –** 5.0 mg/L as PO_4
3. ***Target pH*** • **A –** Target pH of 7.2 • **B –** Target pH of 7.5	4. ***Duplicate Number*** • **1 –** First duplicate • **2 –** Second duplicate

Figure 1 Sample identification legend

METHODS AND PROCEDURES

Eighteen five-gallon buckets of water from the Great Lakes Water Authority (GLWA) was obtained by the City of Flint at the Flint Water Treatment Plant (WTP). The water was shipped to Cornwell Engineering Group (Cornwell) in Newport News, VA. Water remained in the original buckets and was drawn from these buckets at the beginning of every day when water was prepared.

Each coupon was exposed to freshly prepared water twice per week. Half of the coupons were exposed to newly prepared water on Monday and Thursday, with the remaining coupons exposed to newly prepared water on Tuesday and Friday. This usually corresponded to coupons remaining in each batch of water for either three or four days. There were two holidays over the course of the study that resulted in a contact time of seven days. Water preparations consisted of first adding the appropriate amount of phosphoric acid. The chlorine residual was then measured, adjusted and then reconfirmed that the target had been met. The pH was then adjusted using an autotitrator.

After the fresh batch of water was prepared, it was put into a clean coupon jar, the coupons were carefully removed from the old water and placed in the new water. The water in which the samples had been immersed was acidified in the jar that previously held the coupon using a 1:1 nitric acid

(HNO_3) solution. The pH of the acidified samples was confirmed to be below 2 s.u. and allowed to sit for 2 to 3 three days before transferring approximately 100 mL to plastic sample bottles to await analysis. Lead concentration was analyzed by the Cornwell lab using graphite furnace spectroscopy for total lead. Lead results are reported as µg/L-day.

Coupon Apparatus

Glass jars with a volume of approximately 500 mL were used to contain each batch of water, along with the submerged coupon. Acrylic sheets were cut to fit atop each jar. The acrylic sheets were labeled with a Sample ID corresponding to its test conditions, and jars were labeled with matching Sample IDs as well as batch numbers. The lead coupons were machined as thin strips of metal with a hole near one end. Lead coupons were approximately 3 inches in length, ½ inch wide and 1/16 inch thick. The coupons were attached to the acrylic sheets via zip-ties. Before use, the lead coupons were cleaned according to procedures in *Metal Corrosion Coupon Contamination, Corrosion Study Design, and Interpretation Problems* (Lytle et al., 1992)

The jars were completely filled with water to eliminate head space. A silicone sealant was added after batch 11 to cover holes in the acrylic sheet for the zip-ties, so that no water-air interaction could occur.

Corrosion Inhibitor Dosing

Water was tested for residual phosphate using Hach Method 8048. Each jar was then dosed with its corresponding volume orthophosphate stock, minus the residual. The orthophosphate stock was a 1:500 dilution of SLI PHOS-36. Two stock batches were prepared over the course of the study by adding 1 mL of SLI PHOS-36 to 500 mL of deionized water. The newly prepared stock was then tested to ensure acceptable concentration.

Free Chlorine Dosing

Free chlorine was dosed using a 1:100 bleach dilution stock. Stock concentration was measured prior to dosing each morning. The water arrived with no measurable free chlorine residual, and was determined to have a chlorine demand. Thus, the water was dosed with the target residual plus the demand.

pH Adjustment

Adjustment of pH was performed using a Hanna HI902 auto titrator dosing 0.1 N NaOH or 1.0 N H_2SO_4 to reach the determined target pH of either 7.2 or 7.5 s.u.

Figures 2 and 3 show the measured pH in each apparatus following the 3-day or 4-day holding time. With the use of zero headspace, the pH generally did not rise more than 0.2 – 0.3 s.u. above the target pH. There is a large increase in the final pH of Batch 16, which was left submerged for one week. The limited pH drift provided a clear distinction between the two target pH values. So although due to primarily chemical reactions the pH of each condition increased, there were two different pH zones that allowed for a comparison of pH on lead solubility.

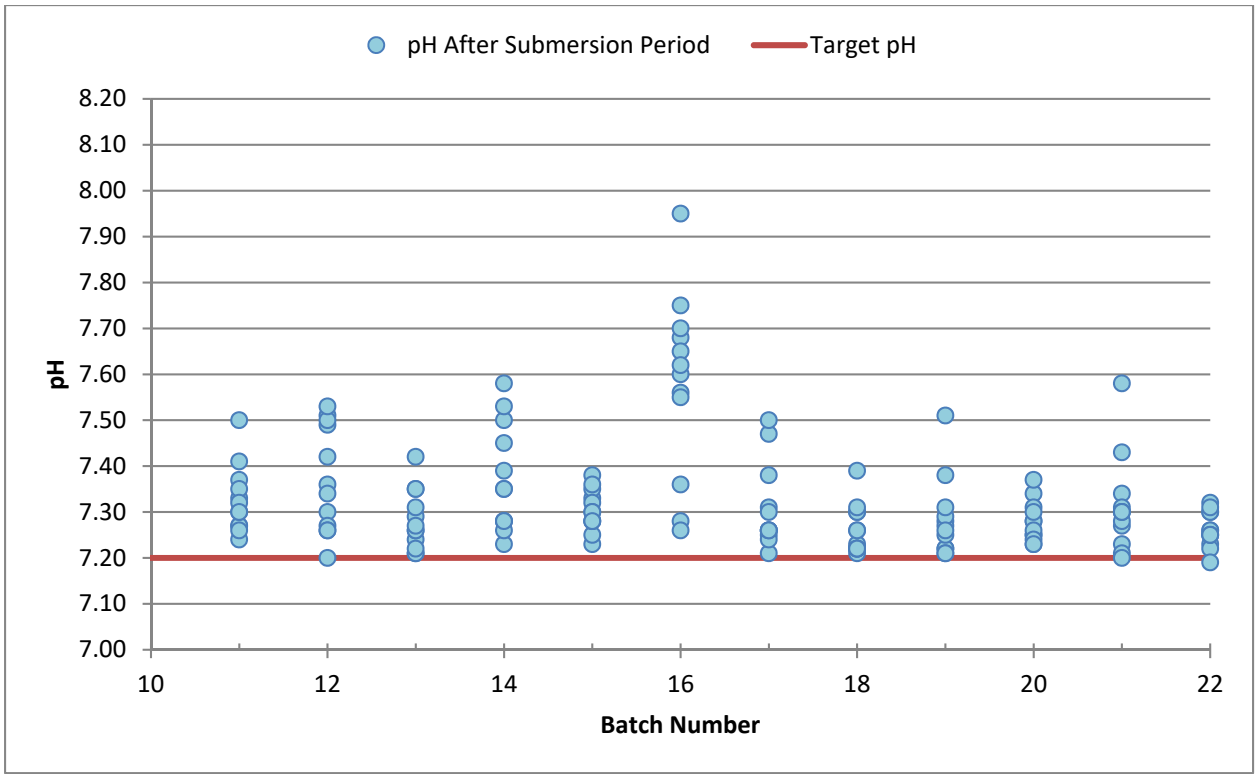

Figure 2 Post-test period pH for batches with an initial pH of 7.2

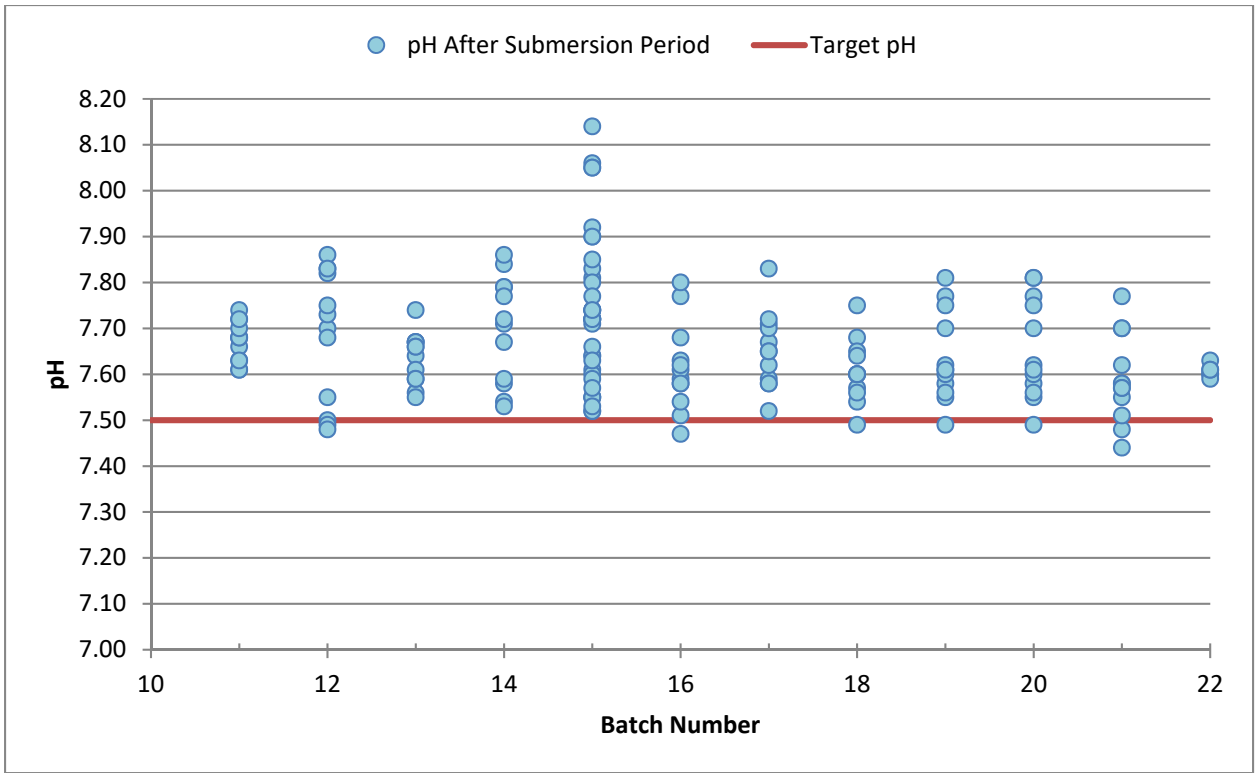

Figure 3 Post-test period pH for batches with an initial pH of 7.5

RESULTS

Sample Analysis

Graphs showing the raw sample data for each coupon are provided in Appendix A. As discussed previously, coupon submersion periods lasted either three, four, or, on two occasions, seven days. Because the duration of each submersion period was variable (either three, four, or seven days), the lead release data were normalized by time. Time-normalized data are plotted in Appendix B.

Outlier points were removed using the interquartile range (IQR) method, which determines outliers from two data sets by iteratively assessing if data points are within the range of the first and third quartile, minus or plus 1.5 times the IQR. Two quartile tests were performed. First, a quartile test was used on the data between when the volume was increased, and when sealant was added, in order to remove obvious outliers. Next, a quartile test was used to remove outliers after steady state had been reached.

The graphs presented in this chapter display the average lead concentration between the duplicates of each test condition, and indicate when steady state was reached with a vertical line.

Orthophosphate Dose Comparisons

Figure 4 and Figure 5 show the six different orthophosphate doses at a target pH of 7.2, and 7.5 respectively. As mentioned above, each data point represents the average of the two duplicates analyzed for that condition. Steady state was deemed to have been achieved after 42 days based on visual observation of the data. In order to better view the corrosion trends, Figures 6 and 7 show only the data after steady state was achieved and use a zoomed in scale on the Y-axis.

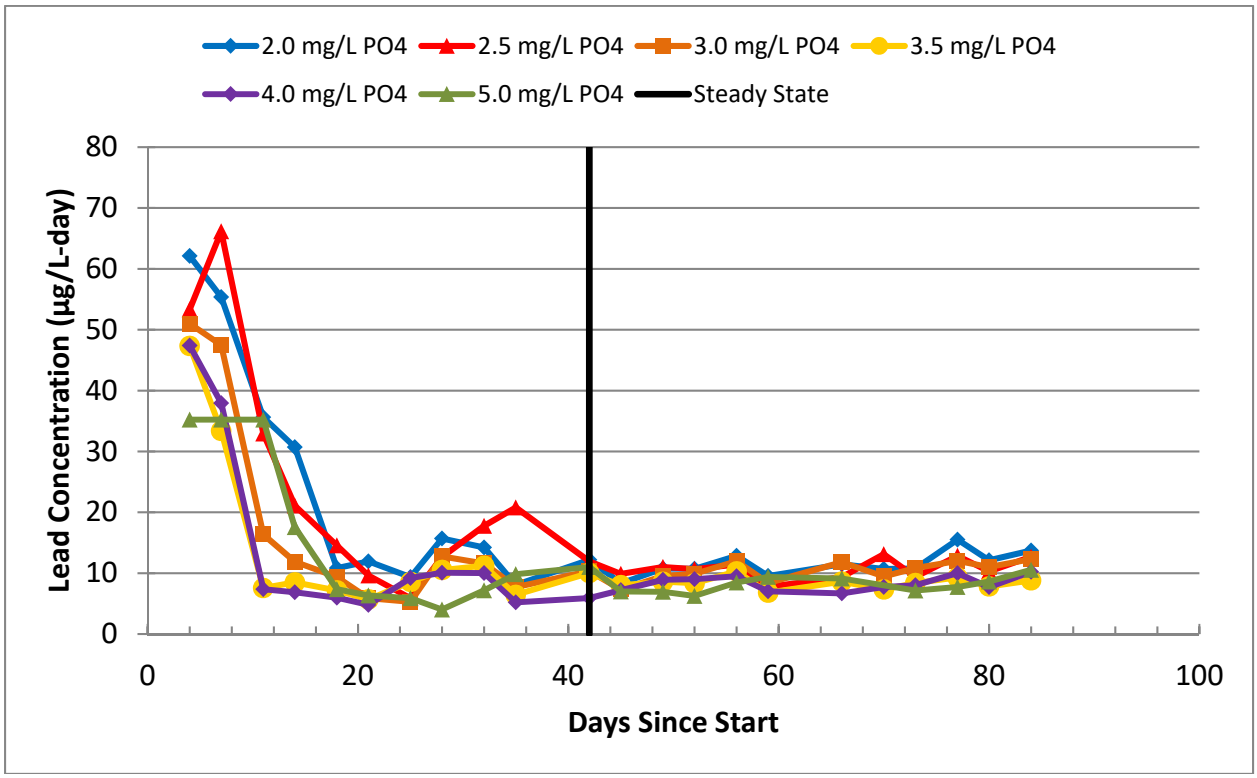

Figure 4 Orthophosphate dose results with a 7.2 pH target

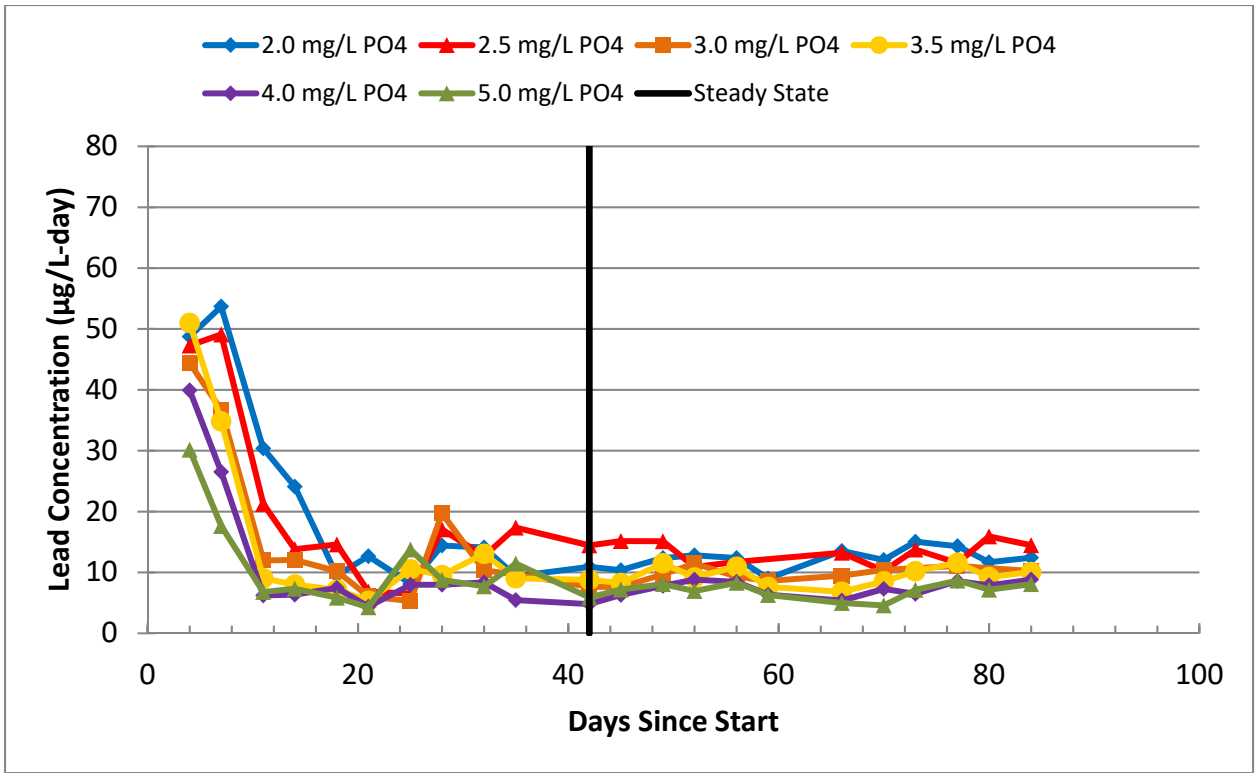

Figure 5 Orthophosphate dose results with a 7.5 pH target

Figure 6 and Figure 7 show the same data as Figure 4 and Figure 5, but only after the coupons were equilibrated to their test conditions, and steady state was achieved. At a pH of 7.2, the 3.5 mg/L, 4.0 mg/L, and 5.0 mg/L as PO_4 doses had very similar lead concentrations. There visually appeared to be some separation of performance at the doses of 2.0, 2.5, and 3.0 mg/L as PO_4 as compared to the 4.0 and 5.0 mg/L as PO_4 doses. At a pH of 7.5, the 4.0 mg/L and 5.0 mg/L as PO_4 doses performed very similarly.

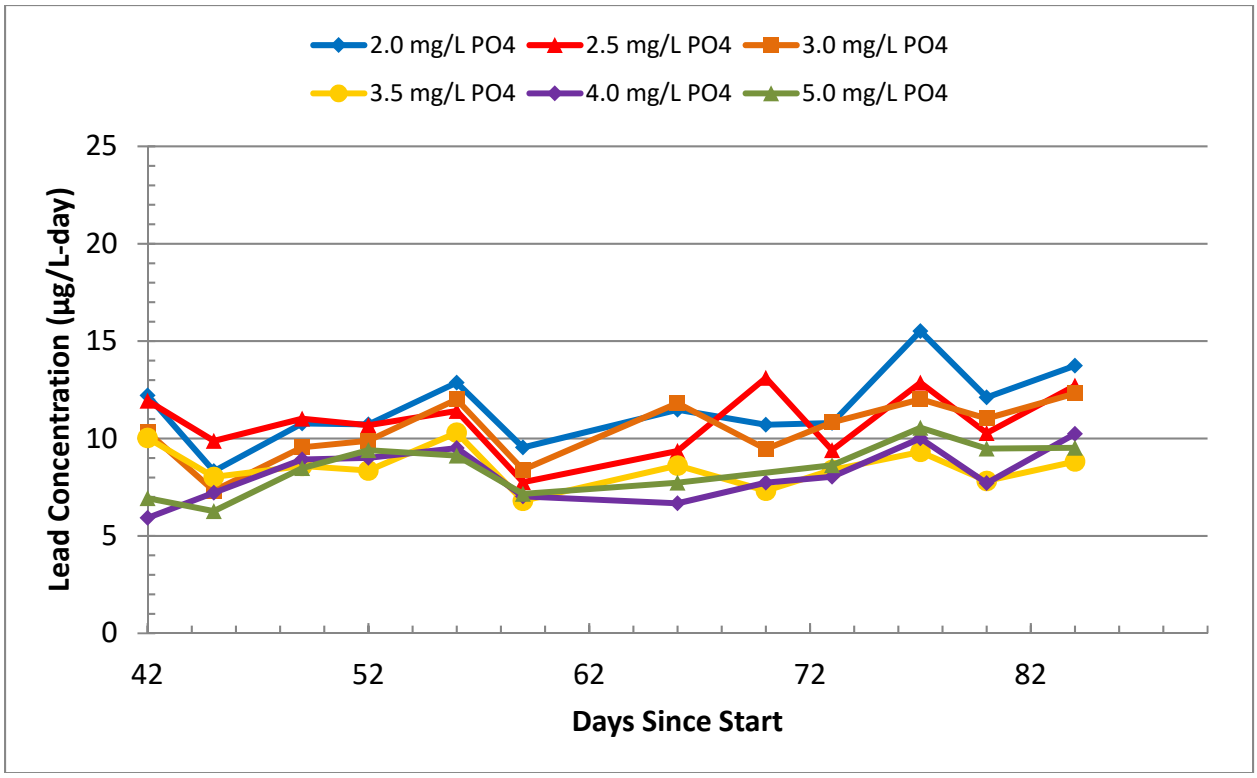

Figure 6 Steady state results for different orthophosphate doses with a 7.2 pH target

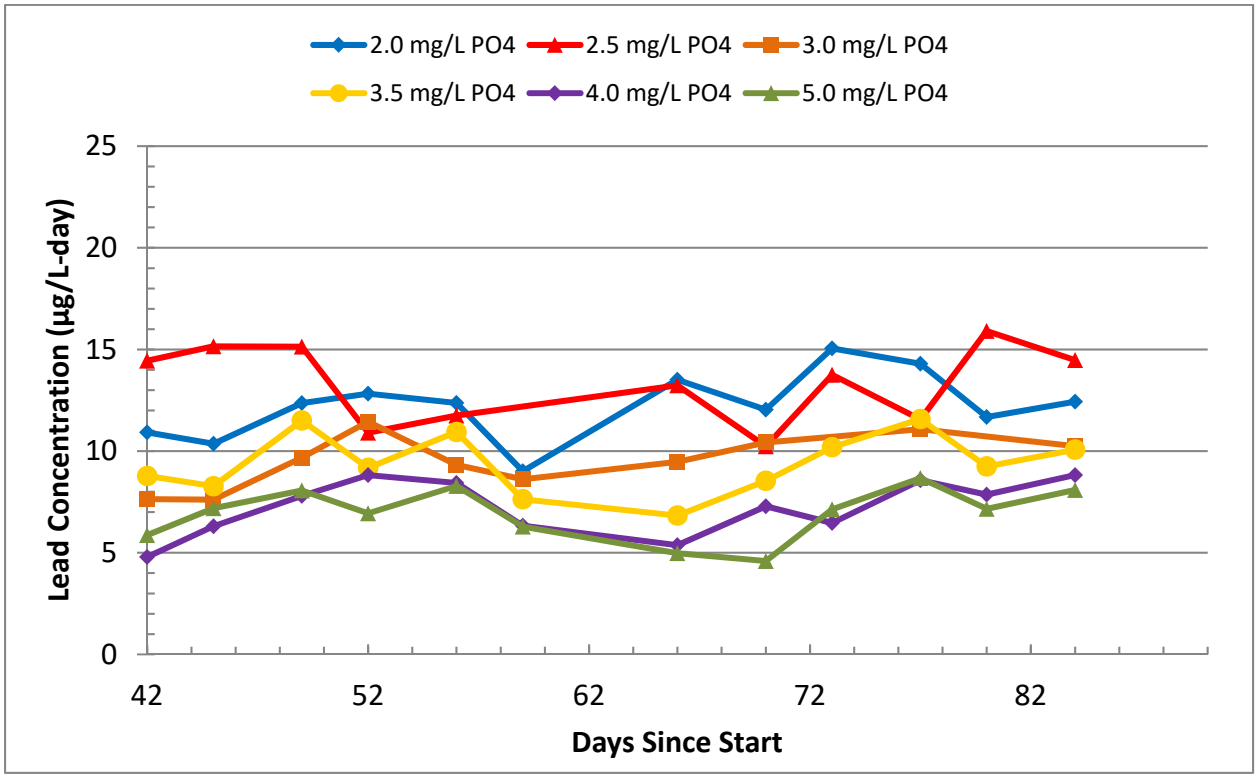

Figure 7 Steady state results for different orthophosphate doses with a 7.5 pH target

Data Analysis

Successively increasing doses were compared at both target pH values. These comparisons are plotted in Appendix D. From these graphs, it is very difficult to determine whether or not there is a difference in the lead trends between pH values of the same orthophosphate dose. The lead levels at most doses actually appear to be so close, further analysis was necessary to determine if there was any significant difference in the lead levels observed at the different pH values for the same orthophosphate dose. Statistical tests were also used to compare the orthophosphate doses.

T-Test Analysis to Compare pH

A t-test assuming unequal variances was performed for several scenarios. The null hypothesis for every test was that the hypothesized mean difference was equal to 0. That is, the lead concentrations were the same. The first test compared averages of the same orthophosphate dose, but different target pH (i.e. F2.0A and F2.0B, etc.) using a significance (α) value of 0.05. This initial test compared the data from the entire study. Every orthophosphate dose supported the hypothesis that the lead results were not statistically different at the two pH values. Table 2 shows the statistics of the pH comparison. Tables 5-10 in Appendix E contain the individual results for each test.

Table 2
Summarized t-test 1 results for pH comparison using all data

Comparison	Mean 1	Mean 2	T Statistic	t Critical (two tail)	Lead is the same
2.0A vs 2.0B	17.85	16.91	0.2308	2.021	SUPPORTED
2.5A vs 2.5B	17.52	16.81	0.1762	2.024	SUPPORTED
3.0A vs 3.0B	13.83	13.10	0.2196	2.021	SUPPORTED
3.5A vs 3.5B	11.31	12.29	0.3232	2.018	SUPPORTED
4.0A vs 4.0B	11.04	9.43	0.5715	2.022	SUPPORTED
5.0A vs 5.0B	9.75	8.95	0.4337	2.021	SUPPORTED

The second scenario used the same null hypothesis, and alpha value of 0.05. This test compared the same sets as the first test, but only used lead data after steady state was reached. The summarized results are seen in Table 3, and individual test results are listed in Appendix E. The null hypothesis was supported for all tests except the 2.5 and 5.0 mg/L as PO_4 doses. By comparing the first and second t-tests, it is concluded that no significant difference exists in the lead levels observed at the different pH values. After this conclusion, the two target pH groups were combined for further analysis.

Table 3
Summarized t-test 2 results for pH comparison after steady state

Comparison	Mean 1	Mean 2	T Statistic	t Critical (two tail)	Lead is the same
2.0A vs 2.0B	11.565	12.239	-0.924	2.074	SUPPORTED
2.5A vs 2.5B	10.870	13.660	-3.550	2.086	REJECTED
3.0A vs 3.0B	10.412	9.554	1.400	2.086	SUPPORTED
3.5A vs 3.5B	8.531	9.398	-1.656	2.093	SUPPORTED
4.0A vs 4.0B	8.166	7.238	1.658	2.074	SUPPORTED
5.0A vs 5.0B	8.482	6.939	2.832	2.080	REJECTED

T-Test Analysis to Compare Orthophosphate Dose

A t-test was performed to determine if there was a significant difference in the lead levels observed at the different orthophosphate doses, after the lead concentrations from both target pH values were averaged for each dose. The same null hypothesis was used, and a significance (α) value of 0.05. A summary of the test results is listed below in Table 4, and individual test results of this test are found in Tables 17-21 in Appendix E. There was a significant difference between the 2.0 and 2.5 mg/L as PO_4 dose, as well as the 4.0 and 5.0 mg/L as PO_4 doses. These doses represent the lowest and highest successive doses, respectively. There was a statistically significant decrease in lead when the orthophosphate dose was increased from 2.5 to 3.0 mg/L as PO_4, from 3.0 to 3.5 mg/L as PO_4, and from 3.5 to 4.0 mg/L as PO_4.

Table 4
Summarized t-test 3 results

Comparison	Mean 1	Mean 2	T Statistic	t Critical (two tail)	Lead is the same
2.0 vs 2.5	11.902	11.864	0.060	2.074	SUPPORTED
2.5 vs 3.0	11.864	10.097	3.074	2.080	REJECTED
3.0 vs 3.5	10.097	8.964	2.377	2.074	REJECTED
3.5 vs 4.0	1.200	1.806	2.521	2.080	REJECTED
4.0 vs 5.0	1.806	1.965	0.274	2.074	SUPPORTED

Graphical Combined pH Data

As previously discussed, t-tests determined that there was no difference in lead corrosion between the target pH values. The averages that were determined previously were then combined with the corresponding averages for the same orthophosphate dose at the other pH condition. The following results were shown using only a two-symbol sample ID, having averaged all coupons of the same orthophosphate dose.

Results of the entire study period are found in Figure 8 below. Once again, it is most useful to view the results after steady state was reached as shown in Figure 9. Most noticeably the 4.0 and 5.0 mg/L as PO_4 doses had very similar trends. The 2.0 and 2.5 mg/L as PO_4 doses also had similar trends but at higher lead levels that the 4 and 5 mg/L as PO_4 doses. As the t-test indicated, there was not a significant difference between either of these two dose comparisons. The difference between the remaining consecutive doses appears to show a decrease in lead. Figure 10 is a dot plot of all the steady state data for the different doses. This dot plot also shows the averages of each coupon for a given orthophosphate dose. The dot plot supports that there was a reduction in lead when the orthophosphate dose was increased from 2.0 to 4.0 mg/L as PO_4, even though there is only a 1 ppb difference in lead released between the doses of 3.5 and 4.0 mg/L as PO_4 and only 2.3 ppb difference in lead between the doses of 3.0 and 4.0 mg/L as PO_4.

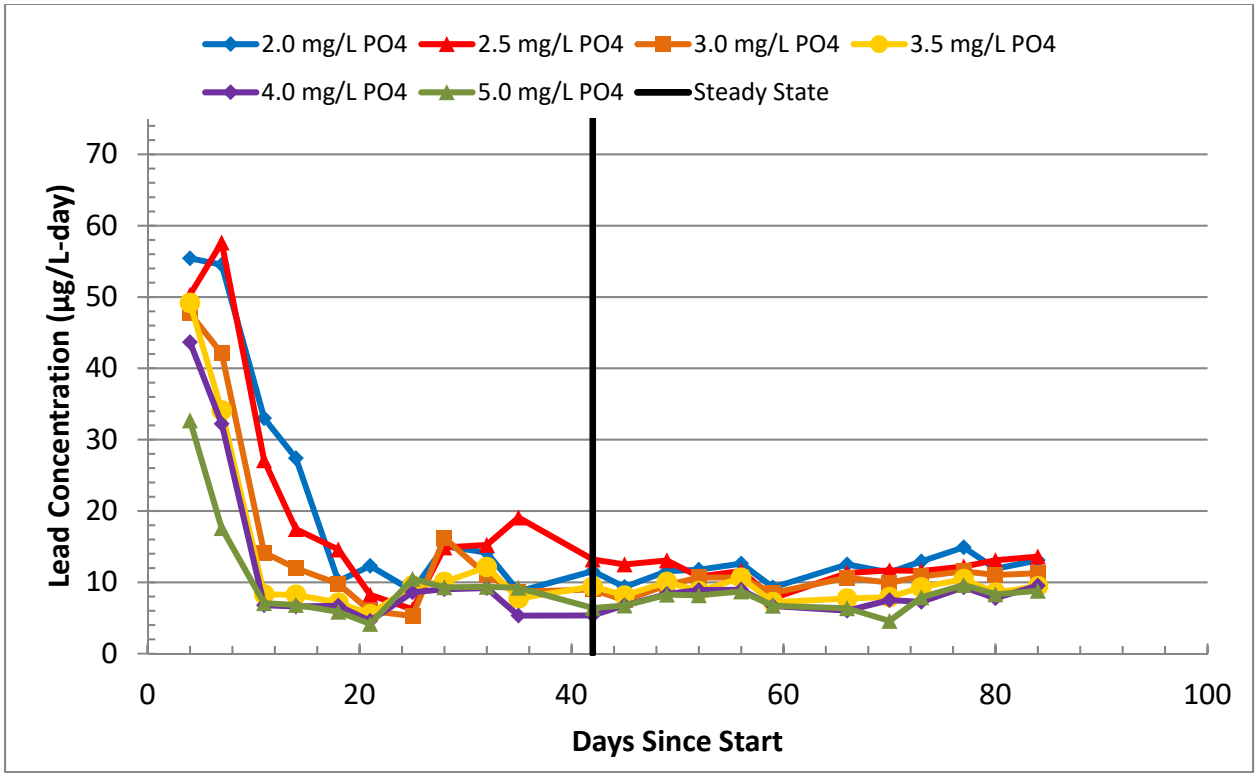

Figure 7 Combined pH results for different orthophosphate doses

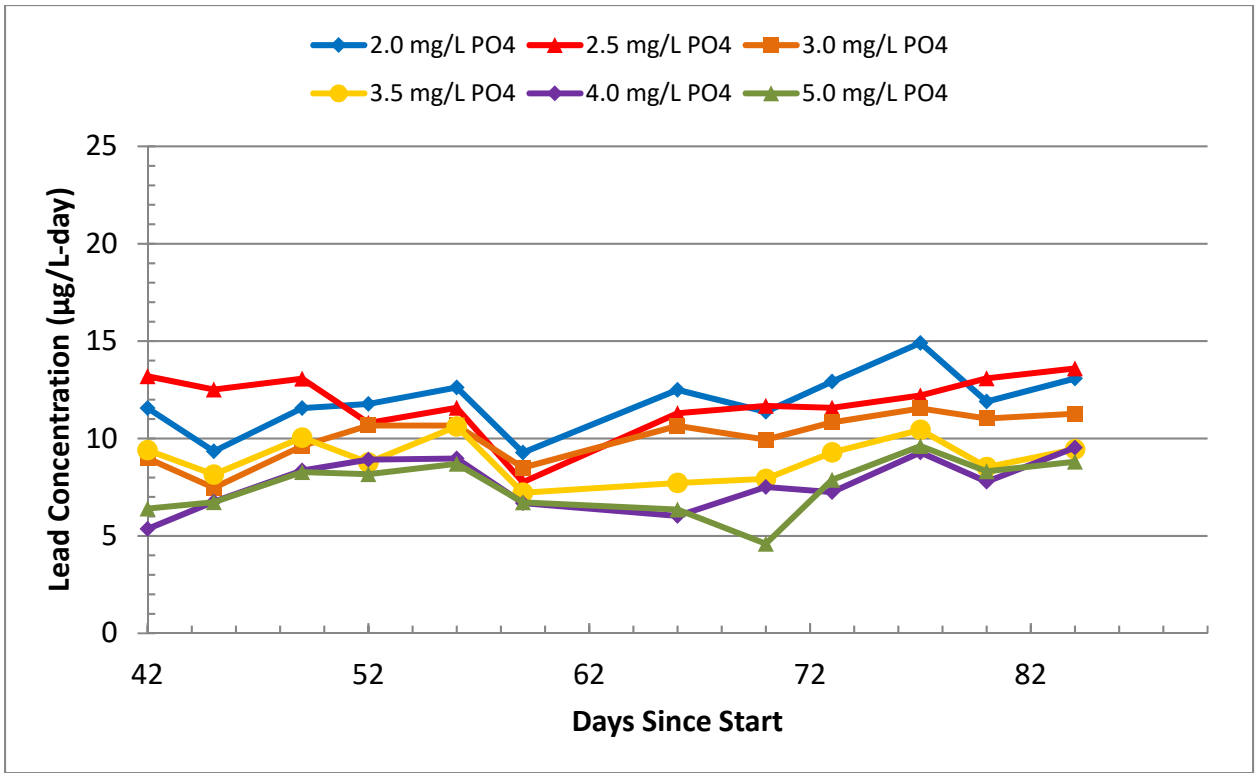

Figure 8 Combined pH results post-steady state for different orthophosphate doses

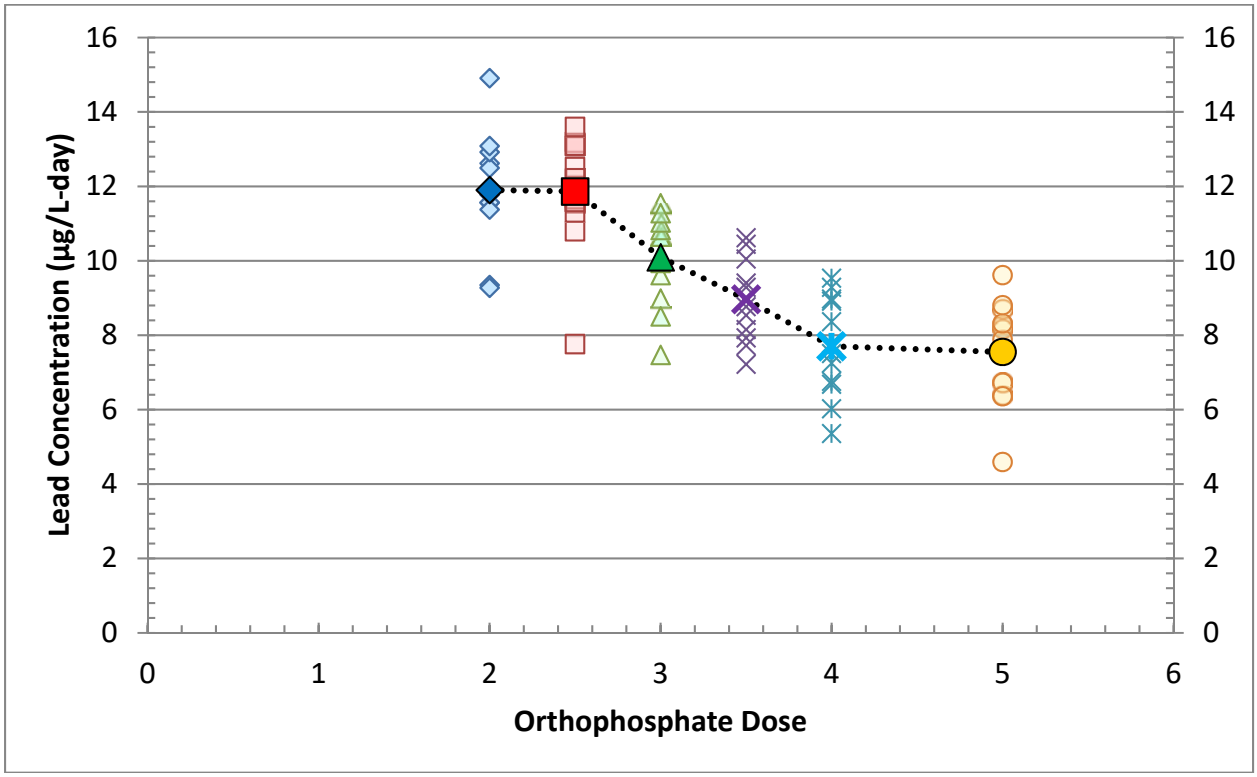

Figure 9 Lead concentrations by orthophosphate dose. Averages are represented with a dotted line.

CONCLUSIONS AND RECOMMENDATIONS

The data presented in this memo have been averaged between duplicates, time-normalized, and have had outliers removed based on the interquartile range to reduce the noise.

In this study, the difference in lead under the two target pH conditions (7.2 and 7.5) was not statistically different. This conclusion is consistent with literature data that shows similar orthophosphate performance in the pH range tested.

The trends show that there is no difference in lead between the 4.0 and 5.0 mg/L as PO_4 orthophosphate doses. Between 2.5 and 4.0 mg/L as PO_4, lead release from the lead coupons consistently decreased with an increase in orthophosphate dose. The lead change in this dose range was small (a few ppb) but statistically and visually different.

The general performance trends of orthophosphate doses will be used to guide a pipe loop study. It is recommended that the pipe loop investigate lead release at different pH levels only as a secondary consideration and if enough pipes are available for testing. The testing of different orthophosphate doses in the loop system should be the prime objective. If possible, doses of 2.0 to 2.5 (since these values were statistically the same a value between the two can be used), 3.0, 3.5, and 4.0 mg/L as PO_4 should be evaluated in a pipe loop study to confirm coupon results. Since GLWA currently has an orthophosphate residual of about 1 mg/L as PO_4, it would be of interest to also test that condition.

REFERENCES

Lytle, D. A., Schock, M. R., & Tackett, S. (1992). Metal corrosion coupon contamination, corrosion study design, and interpretation problems (No. PB-93-194181/XAB; EPA--600/A-93/111). Environmental Protection Agency, Cincinnati, OH (United States). Risk Reduction Engineering Lab.

APPENDIX A – RAW DATA

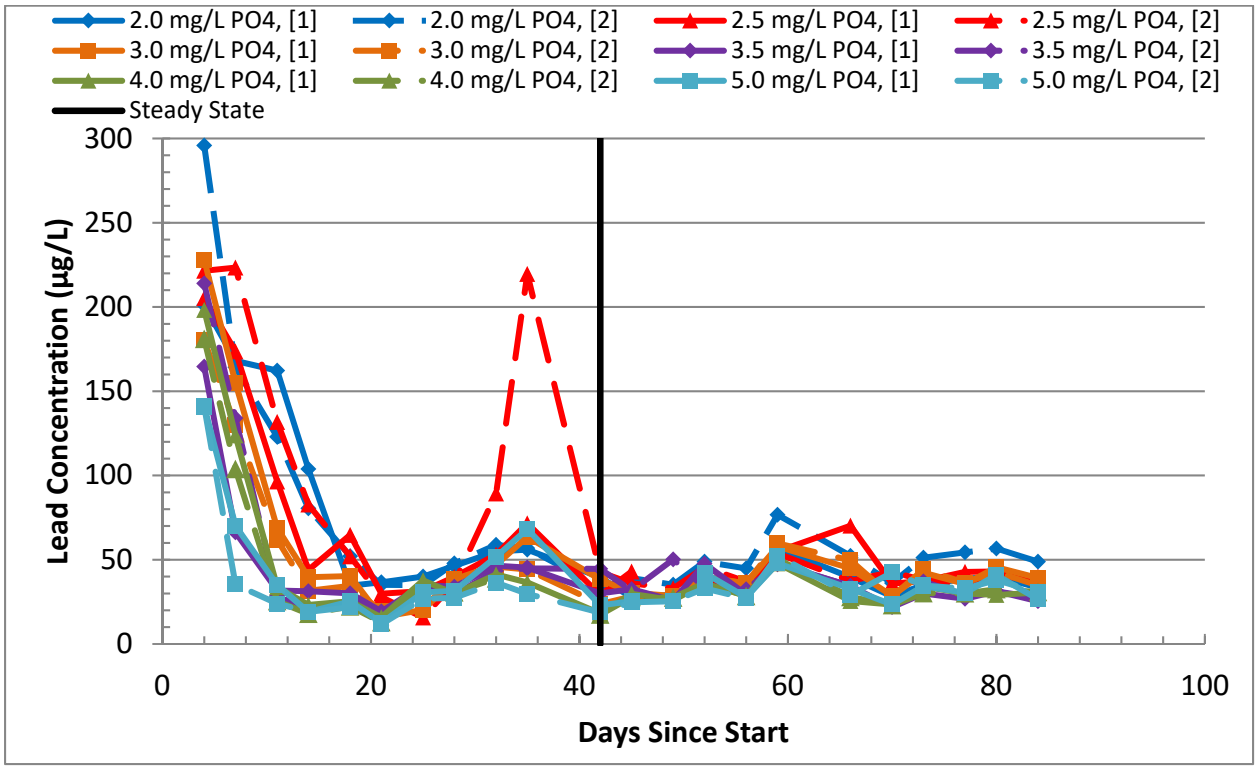

Figure A1 Raw lead release data, pH 7.2

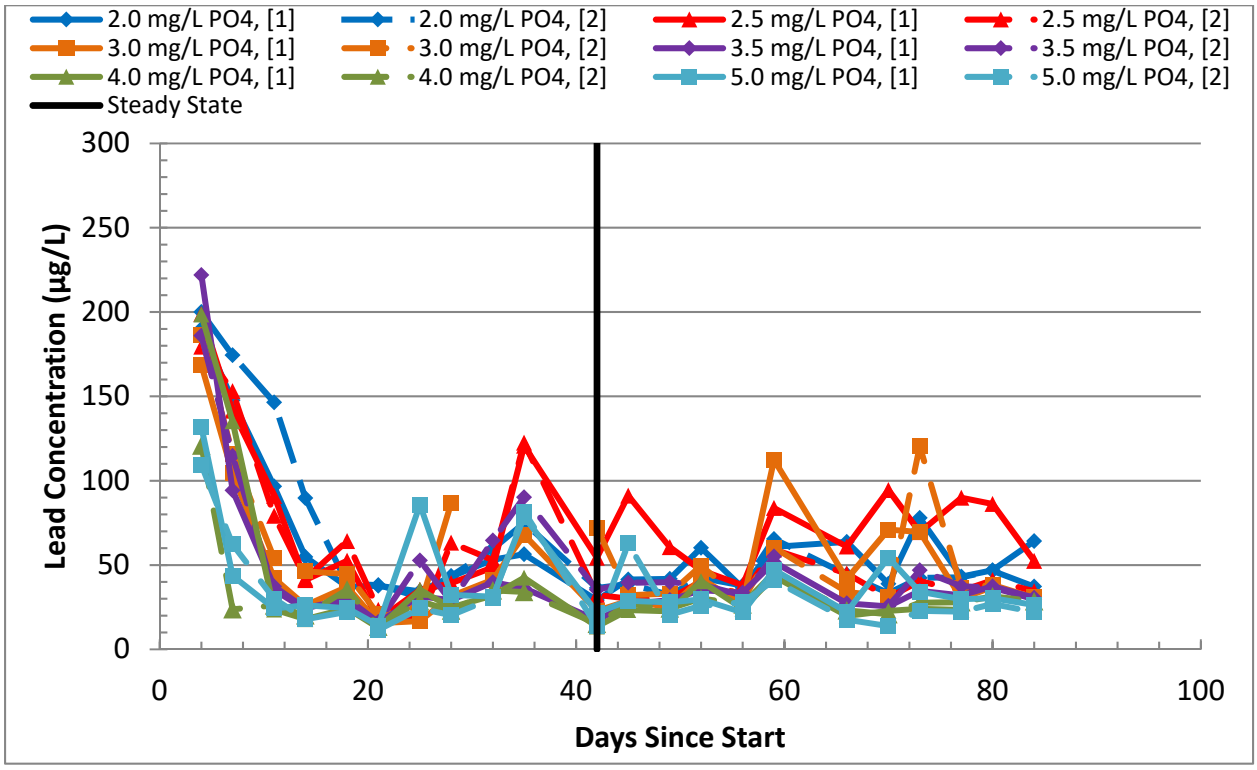

Figure A2 Raw lead release data, pH 7.5

APPENDIX B – NORMALIZED DATA

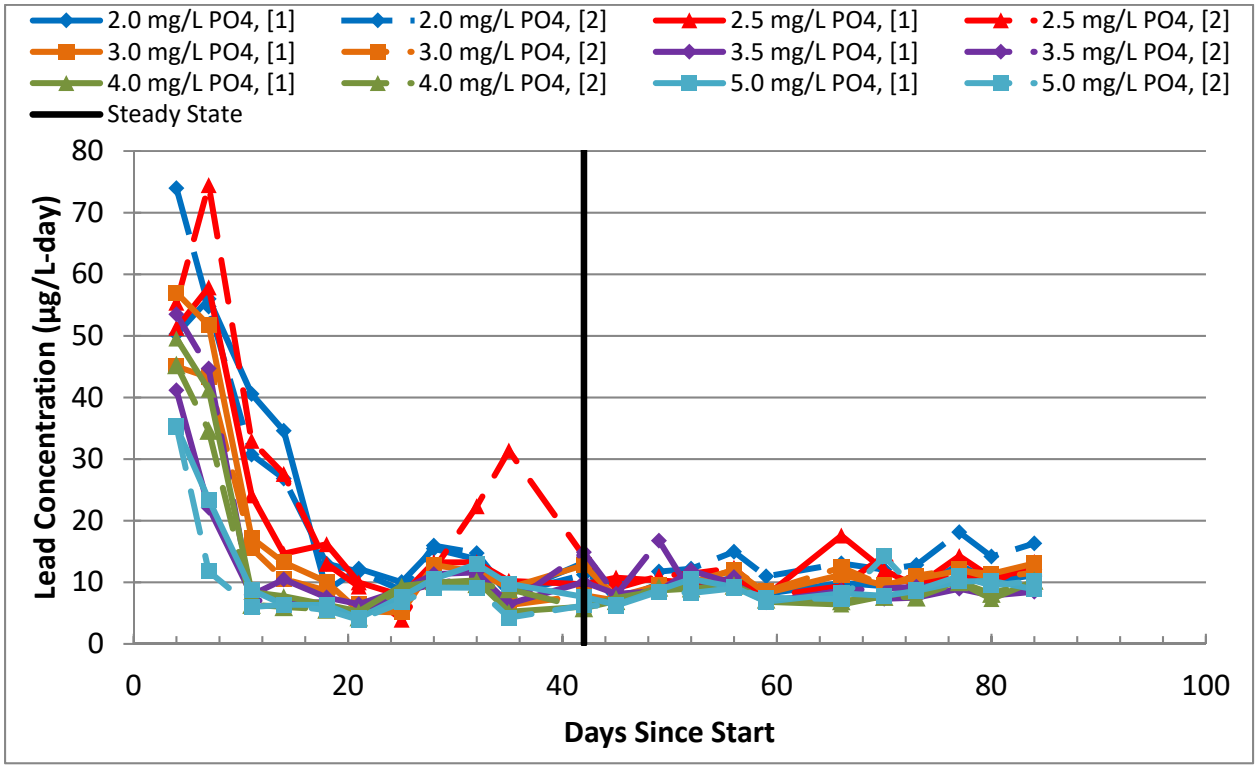

Figure B1 Time normalized lead release data, pH 7.2

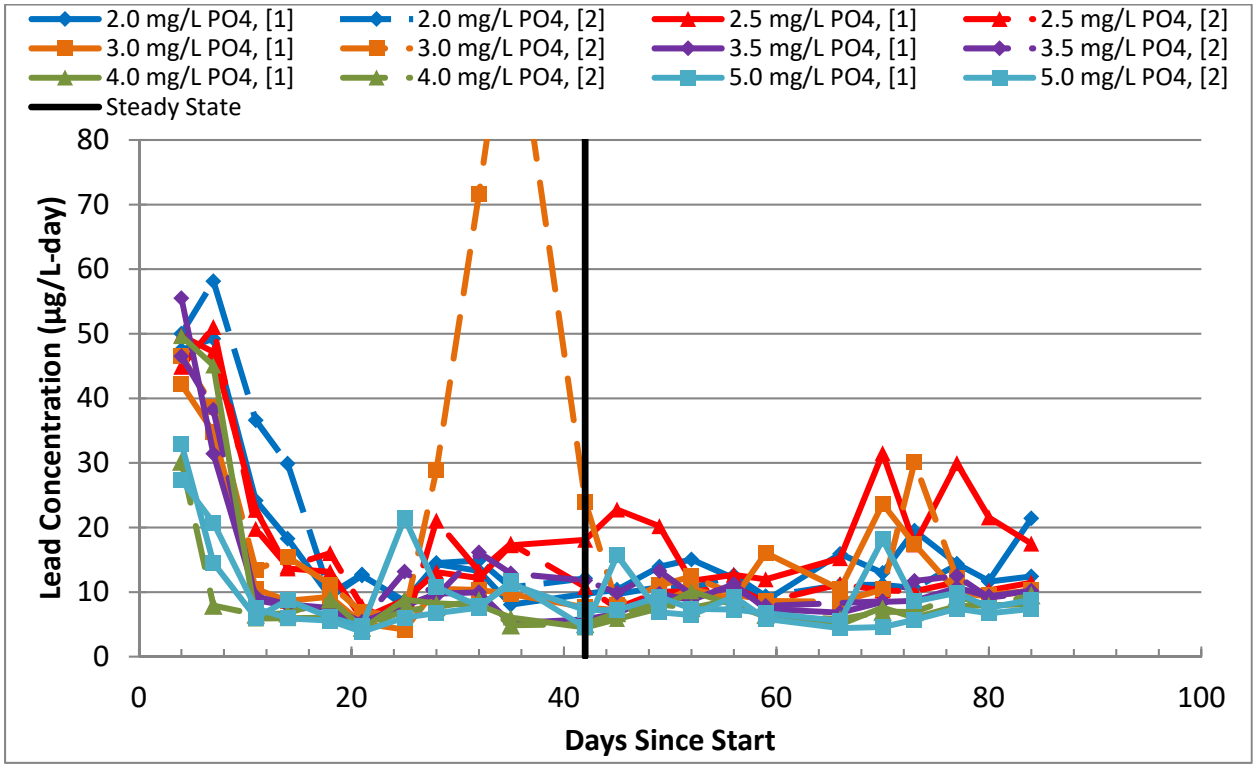

Figure B2 Time normalized lead release data, pH 7.2

APPENDIX C – NORMALIZED DATA AFTER OUTLIER REMOVAL

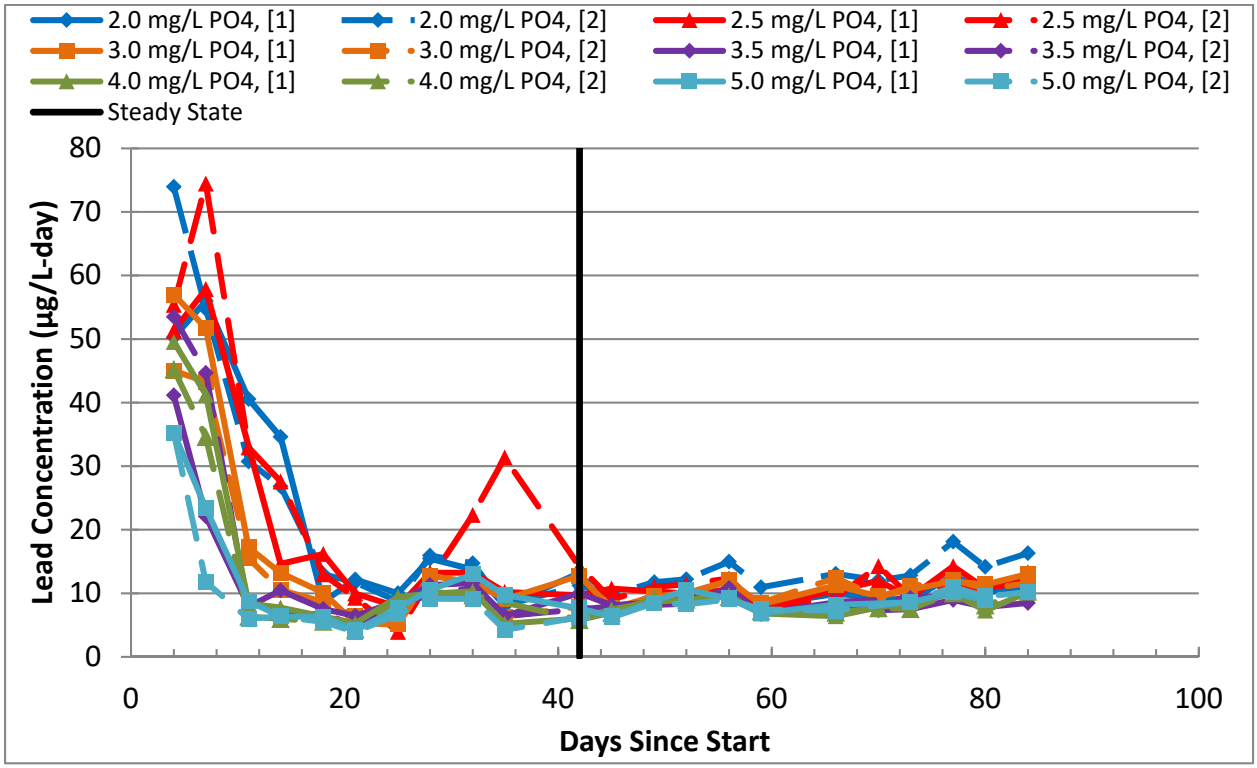

Figure C1 Time normalized lead release data after outlier removal, pH 7.2

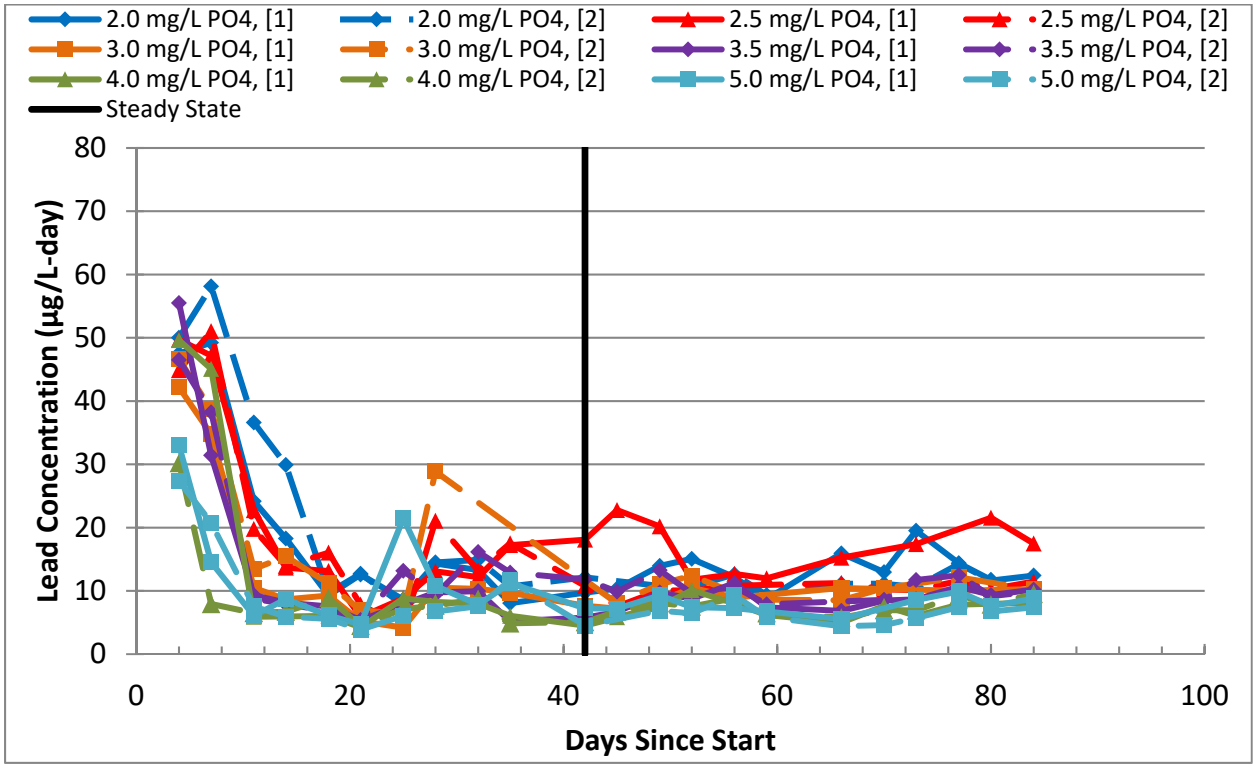

Figure C2 Time normalized lead release data after outlier removal, pH 7.5

APPENDIX D – SEQUENTIAL ORTHOPHOSPHATE DOSAGE COMPARISONS

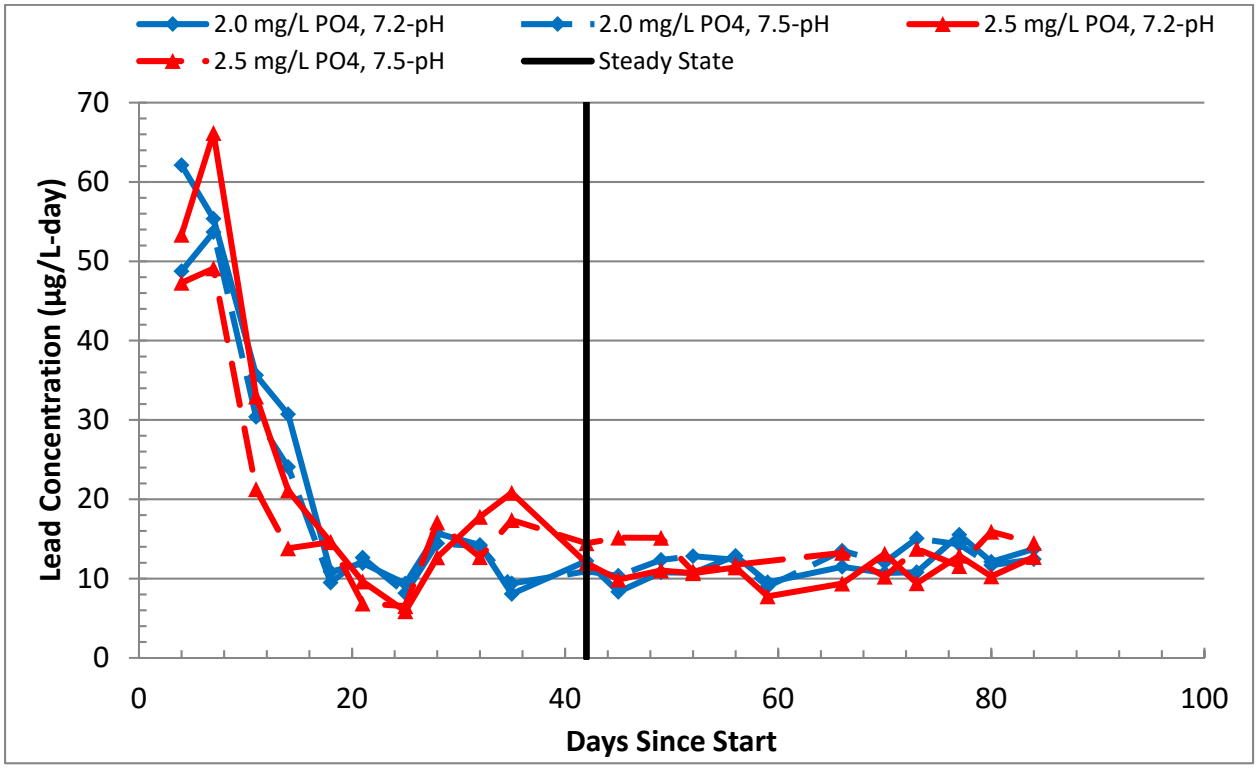

Figure D1 Comparison of lead release under 2.0mg/L vs 2.5mg/L orthophosphate doses

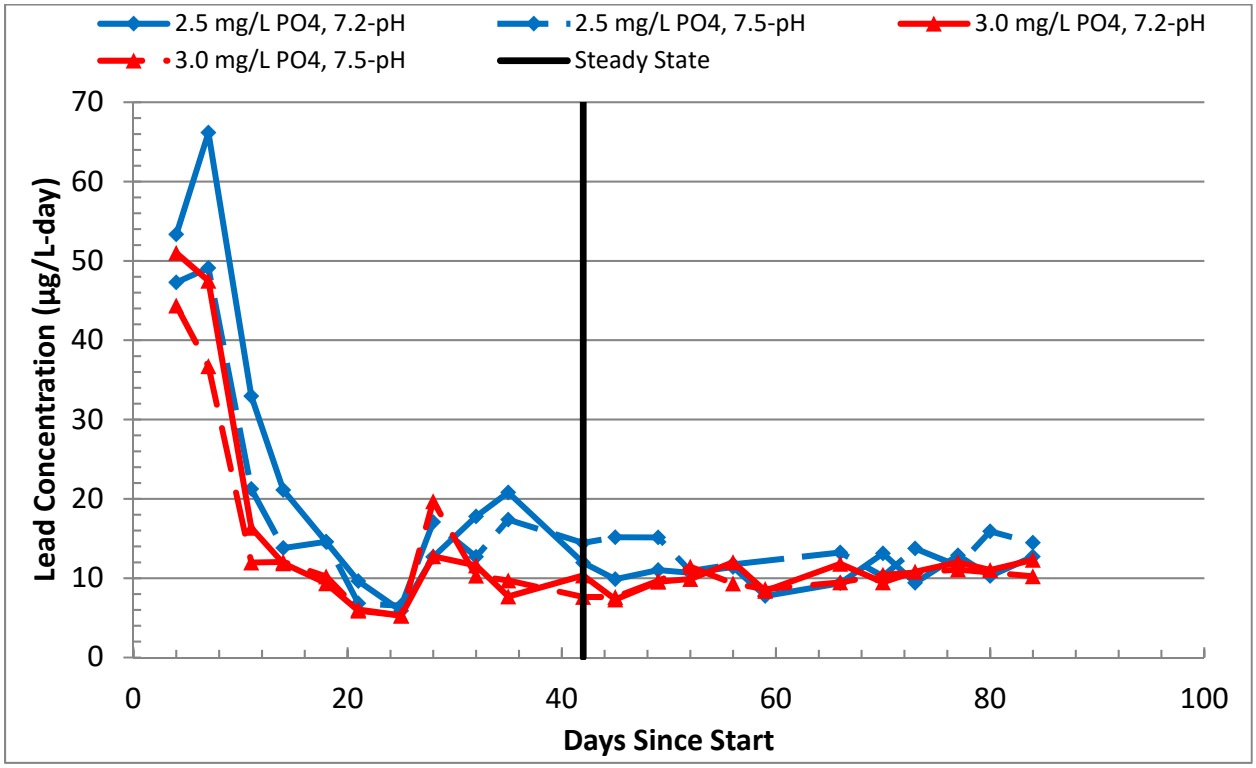

Figure D2 Comparison of lead release under 2.5mg/L vs 3.0mg/L orthophosphate doses

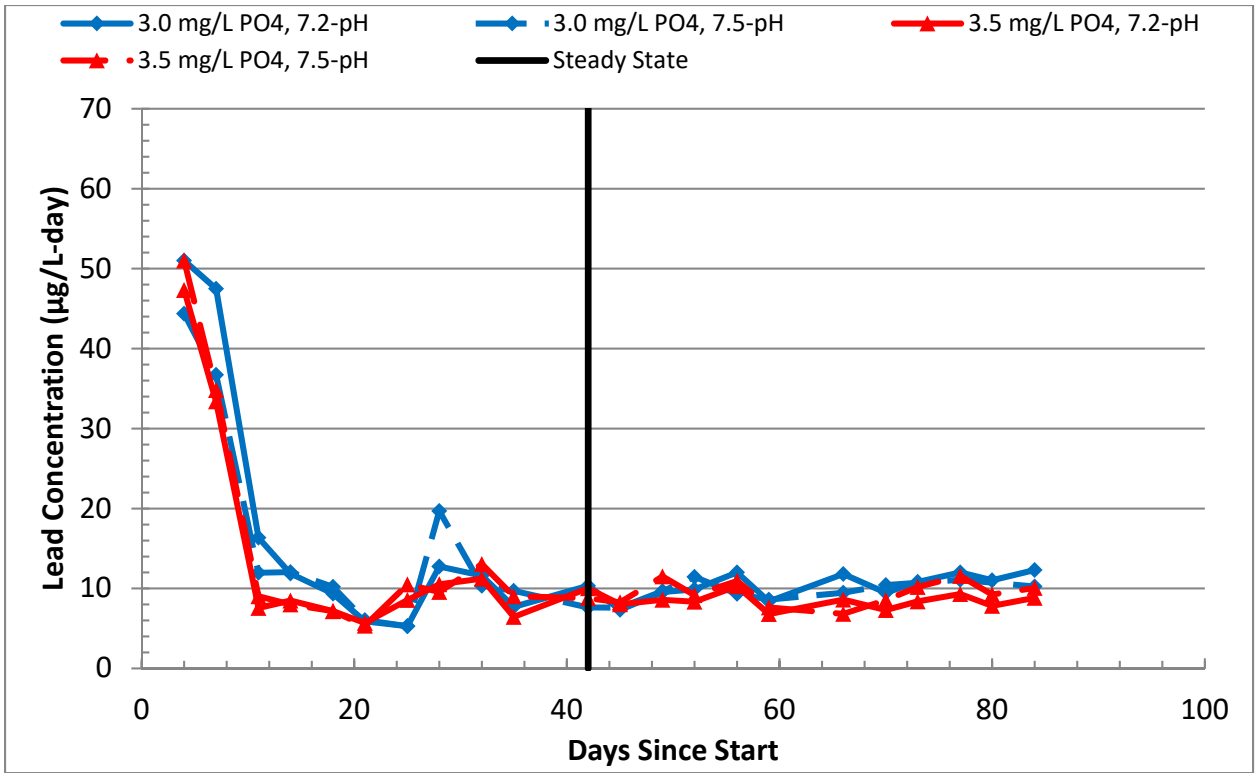

Figure D3 Comparison of lead release under 3.0mg/L vs 3.5mg/L orthophosphate doses

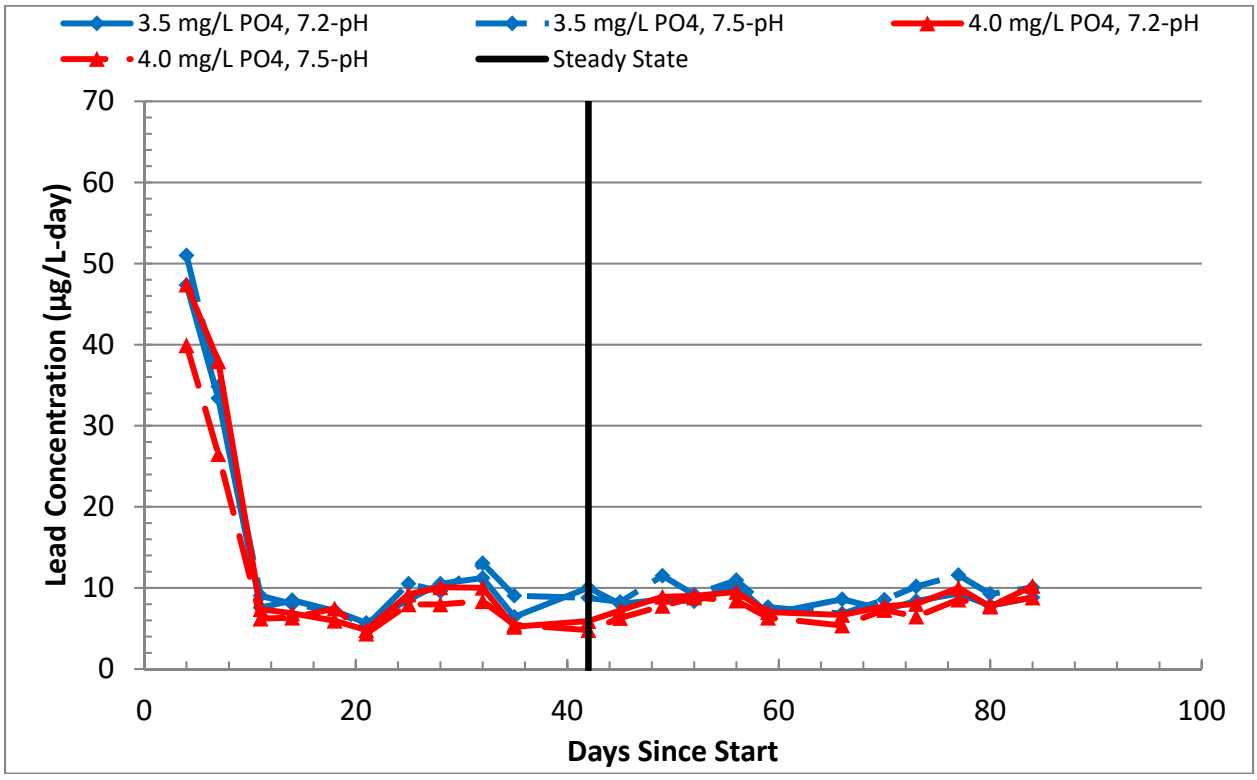

Figure D4 Comparison of lead release under 3.5mg/L vs 4.0mg/L orthophosphate doses

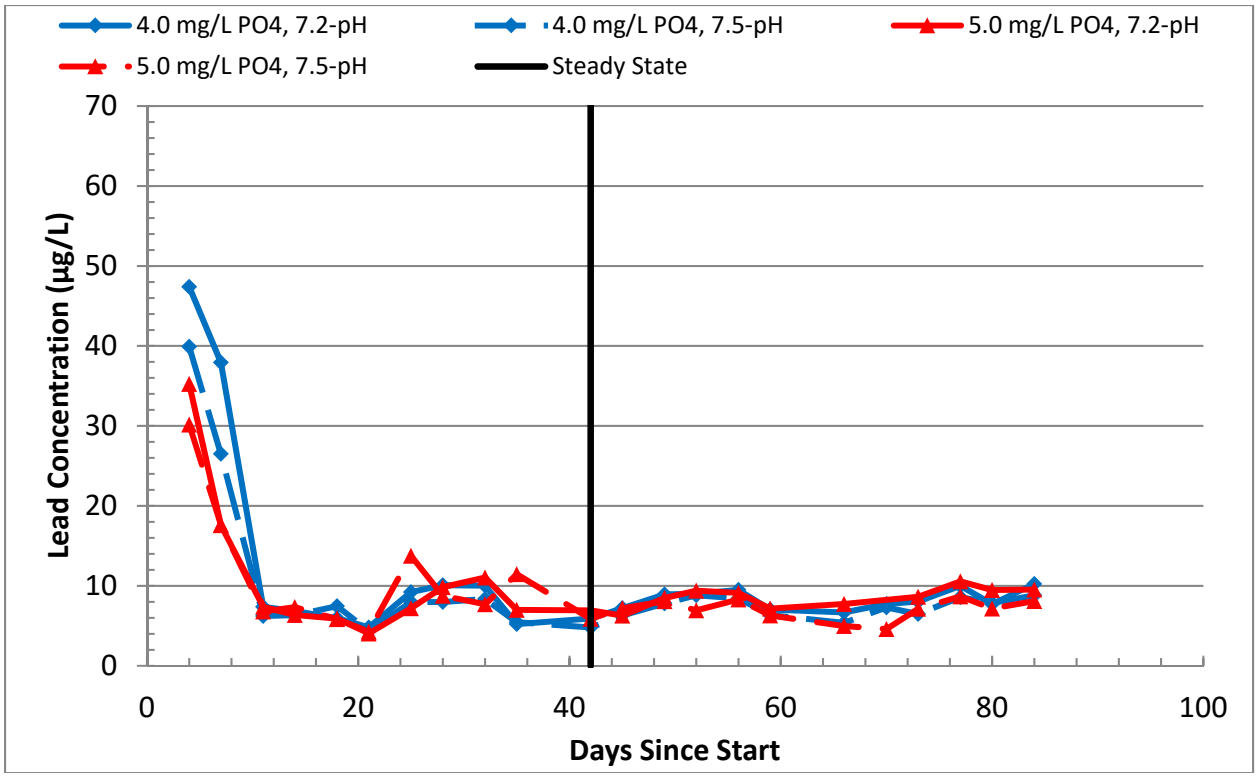

Figure D5 Comparison of lead release under 4.0mg/L vs 5.0mg/L orthophosphate doses

APPENDIX E – T-TEST RESULTS

Table E1
t-Test results for F2.0A and F2.0B lead release data

	F2.0A	*F2.0B*
Mean	17.8523234	16.90726
Variance	220.5744963	148.1653
Observations	22	22
df	40	
t Stat	0.230841062	
P(T<=t) two-tail	0.81861495	
t Critical two-tail	2.02107539	
Null Hypothesis Supported?	TRUE	

Table E2
t-Test results for averaged F2.5A and F2.5B lead release data

	F2.5A	*F2.5B*
Mean	17.51662056	16.81413549
Variance	223.8568139	119.9329405
Observations	22	21
df	38	
t Stat	0.176248051	
P(T<=t) two-tail	0.861035021	
t Critical two-tail	2.024394164	
Null Hypothesis Supported?	TRUE	

Table E3
t-Test results for averaged F3.0A and F3.0B lead release data

	F3.0A	*F3.0B*
Mean	13.82991377	13.09644
Variance	137.7077458	97.95835
Observations	22	20
df	40	
t Stat	0.21958635	
P(T<=t) two-tail	0.827310079	
t Critical two-tail	2.02107539	
Null Hypothesis Supported?	TRUE	

Table E4
t-Test results for averaged F3.5A and F3.5B lead release data

	F3.5A	*F3.5B*
Mean	11.30673015	12.2868
Variance	94.82522864	107.4427
Observations	22	22
df	42	
t Stat	-0.323223404	
P(T<=t) two-tail	0.748129904	
t Critical two-tail	2.018081703	
Null Hypothesis Supported?	TRUE	

Table E5
t-Test results for averaged F4.0A and F4.0B lead release data

	F4.0A	*F4.0B*
Mean	11.03903149	9.428265227
Variance	109.5280199	65.20563213
Observations	22	22
df	39	
t Stat	0.571551788	
P(T<=t) two-tail	0.57090523	
t Critical two-tail	2.02269092	
Null Hypothesis Supported?	TRUE	

Table E6
t-Test results for averaged F5.0A and F5.0B lead release data

	F5.0A	*F5.0B*
Mean	9.752655346	8.952928
Variance	41.31430376	31.52946
Observations	21	22
df	40	
t Stat	0.433680989	
P(T<=t) two-tail	0.666850183	
t Critical two-tail	2.02107539	
Null Hypothesis Supported?	TRUE	

Table E7

t-Test results for averaged equilibrated lead release data: F2.0A and F2.0B

	F2.0A	*F2.0B*
Mean	11.56516865	12.23899
Variance	3.634682719	2.744988
Observations	12	12
df	22	
t Stat	-0.924138641	
P(T<=t) two-tail	0.365440079	
t Critical two-tail	2.073873068	
Support Null Hypothesis?	TRUE	

Table E8

t-Test results for averaged equilibrated lead release data: F2.5A and F2.5B

	F2.5A	*F2.5B*
Mean	10.86988571	13.65977183
Variance	2.672402939	4.739790817
Observations	12	12
df	20	
t Stat	-3.54979863	
P(T<=t) two-tail	0.002009344	
t Critical two-tail	2.085963447	
Support Null Hypothesis?	FALSE	

Table E9

t-Test results for averaged equilibrated lead release data: F3.0A and F3.0B

	F3.0A	*F3.0B*
Mean	10.41189053	9.553839
Variance	2.435846034	1.725668
Observations	12	10
df	20	
t Stat	1.400158012	
P(T<=t) two-tail	0.176788417	
t Critical two-tail	2.085963447	
Support Null Hypothesis?	TRUE	

Table E10

t-Test results for averaged equilibrated lead release data: F3.5A and F3.5B

	F3.5A	*F3.5B*
Mean	8.530813492	9.397693
Variance	1.03017344	2.257861
Observations	12	12
df	19	
t Stat	-1.656080344	
P(T<=t) two-tail	0.114128208	
t Critical two-tail	2.093024054	
Support Null Hypothesis?	TRUE	

Table E11

t-Test results for averaged equilibrated lead release data: F4.0A and F4.0B

	F4.0A	*F4.0B*
Mean	8.166076389	7.238497024
Variance	1.875879781	1.879362199
Observations	12	12
df	22	
t Stat	1.658145888	
P(T<=t) two-tail	0.111479848	
t Critical two-tail	2.073873068	
Support Null Hypothesis?	TRUE	

Table E12

t-Test results for averaged equilibrated lead release data: F5.0A and F5.0B

	F5.0A	*F5.0B*
Mean	8.481883117	6.939152
Variance	1.723018968	1.680982
Observations	11	12
df	21	
t Stat	2.832154634	
P(T<=t) two-tail	0.009982131	
t Critical two-tail	2.079613845	
Support Null Hypothesis?	FALSE	

Table E13
t-Test results for successive doses 2.0 and 2.5 mg/L as PO_4

	F2.0	*F2.5*
Mean	11.90208	11.86432
Variance	2.389849896	2.437484
Observations	12	12
df	22	
t Stat	0.059530092	
P(T<=t) two-tail	0.953067352	
t Critical two-tail	2.073873068	
Support Null Hypothesis?	TRUE	

Table E14
t-Test results for successive doses 2.5 and 3.0 mg/L as PO_4

	F2.5	*F3.0*
Mean	11.86432281	10.09733663
Variance	2.437484149	1.526474729
Observations	12	12
df	21	
t Stat	3.074391747	
P(T<=t) two-tail	0.005752254	
t Critical two-tail	2.079613845	
Support Null Hypothesis?	FALSE	

Table E15
t-Test results for successive doses 3.0 and 3.5 mg/L as PO_4

	F3.0	*F3.5*
Mean	10.09733663	8.964253
Variance	1.526474729	1.200082
Observations	12	12
df	22	
t Stat	2.377087161	
P(T<=t) two-tail	0.026571138	
t Critical two-tail	2.073873068	
Support Null Hypothesis?	FALSE	

Table E16
t-Test results for successive doses 3.5 and 4.0 mg/L as PO_4

	F3.5	*F4.0*
Mean	8.964253472	7.702287
Variance	1.200082422	1.806366
Observations	12	12
df	21	
t Stat	2.521225498	
P(T<=t) two-tail	0.019845596	
t Critical two-tail	2.079613845	
Support Null Hypothesis?	FALSE	

Table E17
t-Test desults for successive doses 4.0 and 5.0 mg/L as PO_4

	F4.0	*F5.0*
Mean	7.702286706	7.548494544
Variance	1.806365605	1.965460158
Observations	12	12
df	22	
t Stat	0.274314659	
P(T<=t) two-tail	0.78640214	
t Critical two-tail	2.073873068	
Support Null Hypothesis?	TRUE	