Supporting Information for

# The Ability of Phosphate to Prevent Lead Release from Pipe Scale when Switching from Free Chlorine to Monochloramine

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Supporting Information contains 60 pages with 12 Sections, 24 Figures, and 4 Tables

## 1 Contents

2	Section S1.	Specific Information about Pipe Loop System	S10
3	Section S2.	Chemical Reagents and Artificial Tap Water Compositions	S14
4	Section S3.	Sample Collection and Pretreatment	S16
5	Section S4.	0-hr Samples: Fresh Tap Water in Carboys	S18
6	Section S5.	Analysis of Water Samples	S19
7	Section S6.	Solid Characterization: Sample Preparation and Analyses	S21
8	Section S7.	Conditioning Lead Pipe Assemblies for First 50 Weeks	S24
9	Sectio	on S7-1. Lead Concentrations during the Conditioning Period (0-50 weeks)	S24
10	Sectio	on S7-2. Water Chemistry during the Conditioning Period	S28
11	Sectio	on S7-3. Scale Analysis: Scanning Electron Microscopy at Weeks 15 and 35.	S29
12	Sectio	on S7-4. Results from Raman Spectroscopy: Weeks 15 and 35	S33
13	Section S8.	Lead Concentrations of 8-hr Samples (Lead Pipe Segment Stagnation	
14		Samples)	S35
15	Section S9.	The pH Increase Associated with Lead Oxidation	<b>S</b> 41
16	Section S10.	Amounts of Phosphorus Deposited in the Scales	S43
17	Section S11.	Mineralogical Scale Characterization	S46
18	Sectio	on S11-1. Before the Disinfectant Switch: Weeks 62 and 72	S46
19	Sectio	on S11-2. After the Disinfectant Switch: Week 83	S49
20	Sectio	on S11-3. After the Disinfectant Switch: Week 95	S49
21	Section S12.	Composition of Outer and Inner Layer of Scale from Week 95-1D	S56

## 22 Figures

23 24 25 26 27 28	Figure S1.	The pe-pH diagram of Washington D.C., tap water. Here, the total dissolved Pb concentration was $5 \times 10^{-7}$ M, the free chlorine concentration was $9.6 \times 10^{-4}$ M, total dissolved inorganic carbon concentration was $1.57 \times 10^{-3}$ M, and the chloride concentration was $1.4 \times 10^{-5}$ M. The oxidation potential of PbO <sub>2(s)</sub> is higher than the H <sub>2</sub> O/O <sub>2</sub> boundary. Thermodynamic values were obtained from diverse studies. <sup>1-3</sup> Thermodynamic values of key compounds are given in Table S1 S6
29 30 31 32 33	Figure S2.	Equilibrium lead solubility of three different lead-containing solids. All calculations were performed for a tap water system with 1.57 mM dissolved inorganic carbon. The calculations were performed by using equilibrium constants from several sources. <sup>2,4</sup> Equilibrium expressions and their equilibrium constants are given in Table S2
34 35	Figure S3.	Photographs of (a) overall pipe reactors and (b) components of each pipe assembly with cut lead pipe segments
36	Figure S4.	Example of weekly timeline of the operation of the pipe loops
37 38	Figure S5.	Lead concentrations of synthetic tap water before it flows through the lead pipe assemblies (0-h samples)
39 40	Figure S6.	Approach for preparing pipe samples for analysis and the associated analyses performed on cross sections and inner pipe surfaces
41 42 43 44 45 46 47 48	Figure S7.	Overall profiles of pipe assemblies during conditioning and the main experiment for (a) total lead concentrations, (b) chlorine concentrations, (c) pH, and (d) phosphate concentrations. Here, Loops 1, 2, and 3 had phosphate pre-addition (starting in Week 66) before the disinfectant switch, while Loops 4, 5, and 6, did not have phosphate added at all. In Week 80, all six pipe assemblies switched disinfectant from free chlorine to monochloramine. In Week 33, manganese was mistakenly added once to the carboys for all six pipe loops. Phosphate concentration was determined by ICP-MS by measuring P
49 50 51	Figure S8.	Dissolved lead concentrations from 168-hour carboy samples during lead pipe system conditioning. In Week 33, there was one day in which manganese, instead of magnesium, was added to the synthetic tap water
52 53 54	Figure S9.	Optical images taken from the half cylinder's inner surface (upper), and scanning electron micrographs from cross-section disk (lower): (a) Week 15 and (b) Week 35
55 56 57 58	Figure S10.	Raman spectra of pipe scale on new lead pipe from (a) Week 15 and (b) Week 35. Peaks corresponding to particular phases are noted. In panel b, multiple peaks are recorded from various spots on surface of each half-cylinder. Each 'White-yellow fluffy phases', 'Bright white with fine blades', 'Mixture of red and gray', and 'Baiaed and area' is indicated on the picture of Figure S11.

60 61	Figure S11.	Optical images taken from the locations where Raman spectra were obtained on the inner surface of a pipe segment from Week 35
62 63 64 65	Figure S12.	Profiles of pipe loops from solutions that had stagnated in the lead pipe assembly for 8 hours (8-h samples): (a) total lead concentration, (b) chlorine concentration, (c) pH, and (d) orthophosphate concentration. Experimental details are identical to those of the 168-h samples which were indicated in Fig. 3
66 67 68 69	Figure S13.	Dissolved lead concentrations of the water that had stagnated in the lead pipe assembly for 8 hours. Dissolved lead concentrations were measured starting in Week 15. In Week 33, there was one day in which manganese instead of magnesium was added to the synthetic tap water
70 71 72	Figure S14.	Total (a) and dissolved lead concentrations (b) from samples taken from pipe loops during the weekly recirculation. Here, the carboys were exchanged with fresh ones at the end of each week
73 74 75 76 77 78 79 80 81 82	Figure S15.	Total and dissolved phosphate concentrations of Loops 1, 2, and 3 for the samples collected at the end of each week. The thick green line indicates the average total phosphate concentrations from freshly prepared carboys (0-hr samples). Phosphate was added starting in Week 66 (indicated by red dotted line). In Week 80, the disinfectant for all six assemblies was switched from free chlorine to monochloramine (indicated by vertical purple dashed line). The phosphate concentration was determined using ICP-MS by measuring P. The phosphate consumption tendency was widely varied among the loops. Before Week 80, Loop 2 showed much higher phosphate consumption than Loops 1 and 3. After Week 80, Loop 1 showed higher consumption than the other two
83 84	Figure S16.	Visual images from the surface of the pipe segment from Week 95-1D (with phosphate) (upper) and Week 95-6D (without phosphate) (lower)
85 86 87 88	Figure S17.	X-ray diffraction patterns of scale scrapings from a pipe at (a) Weeks 62 (without phosphate), (b) 72 (with phosphate), (c) 83 (without phosphate), and (b) 83 (with phosphate). Here, P is $\beta$ -PbO <sub>2(s)</sub> , S is $\alpha$ -PbO <sub>2(s)</sub> , C is cerussite, and Pb <sup>0</sup> is unaltered lead. Panels (c) and (d) are illustrated in next page
89 90	Figure S18.	X-ray diffraction patterns of scale scrapings from a pipe without phosphate at week 95 (95w-6D). Here, C is cerussite, and P is $\beta$ -PbO <sub>2(s)</sub>
91 92	Figure S19.	X-ray diffraction patterns of scale scrapings from a pipe with phosphate at week 95 (95w, Loop 1): (a) outer scale, and (b) inner scale
93 94	Figure S20.	Total Ca concentrations of 168-h samples. The blue dotted line indicates the initial Ca concentration of freshly prepared synthetic tap water
95 96 97	Figure S21.	Results of energy dispersive X-ray spectroscopic analysis of inner surface of lead pipe segment at Week 72. Compositional information within the indicated square or rectangle regions in the SEM figures was obtained and expressed as the relative

98 99 100		(%) atomic proportion of each element. SEM images were taken from two different spots of cross-section of the pipe scale in order to provide sufficient compositional information of the scale
101 102 103 104	Figure S22.	Results of energy dispersive X-ray spectroscopic analysis of inner surface of lead pipe segment of Weeks 83 and 95. Compositional information within the indicated square or rectangle regions in the SEM figures was obtained and expressed as the relative (%) atomic proportion of each element
105 106 107 108	Figure S23.	Results of energy dispersive X-ray spectroscopic analysis of inner surface of Week 95 (with phosphate) lead pipe segment. Composition information within the indicated red square regions in the SEM figures was obtained and expressed as the relative (%) atomic proportion of each element (i.e., Pb, O, and C)
109 110	Figure S24.	Mapping image (SEM/EDS) from the surface of the pipe segment from Week 95- 6D (without phosphate)
111	Tables	
113 114	Table S1.	Thermodynamic values (i.e., Gibbs free energies) for key solids or aqueous species. The values are taken from various sources
115 116 117 118	Table S2.	Reactions and their equilibrium constants for key aqueous species in the pipe loop system. Constants are taken from various sources. The equilibrium constant for Reaction 16 was calculated from molar Gibbs free energies of each component of the reaction
119	Table S3.	Composition of synthetic Washington, D.C., tap water
120 121 122	Table S4.	Comparing total lead concentrations after disinfectant switch. Here, the concentration values in the table are the average of three pipe loops for each condition
123		
124	References	
125		



Figure S1. The pe-pH diagram of Washington D.C., tap water. Here, the total dissolved Pb concentration was  $5 \times 10^{-7}$  M, the free chlorine concentration was  $9.6 \times 10^{-4}$  M, total dissolved inorganic carbon concentration was  $1.57 \times 10^{-3}$  M, and the chloride concentration was  $1.4 \times 10^{-5}$ M. The oxidation potential of PbO<sub>2(s)</sub> is higher than the H<sub>2</sub>O/O<sub>2</sub> boundary. Thermodynamic

- values were obtained from diverse studies.<sup>1-3</sup> Thermodynamic values of key compounds are
- 133 given in Table S1.



Figure S2. Equilibrium lead solubility of three different lead-containing solids. All calculations
were performed for a tap water system with 1.57 mM dissolved inorganic carbon. The
calculations were performed by using equilibrium constants from several sources.<sup>2,4</sup> Equilibrium
expressions and their equilibrium constants are given in Table S2.

No.	Solids or Aqueous Species	$\mathrm{G}^{0}_{f}$ (kJ mol <sup>-1</sup> )	Source
1	PbCO <sub>3(s)</sub>	-625.5	1
2	Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2(s)</sub>	-1699.8	3
3	PbO <sub>2(s)</sub>	-601.2	1
4	$Pb^0$	0	1
5	Pb <sup>2+</sup>	-24.4	1
6	PbOH <sup>+</sup>	-226.3	1
7	Pb(OH) <sub>3</sub> -	-575.7	1
8	HOCl <sub>(aq)</sub>	-79.9	1
9	OC1-	-36.8	1
10	Cl	-131.3	1
11	NH <sub>2</sub> Cl <sub>(aq)</sub>	73.1	4
12	$\mathrm{NH_{4}^{+}}$	-79.4	1
13	NH <sub>3(aq)</sub>	-26.6	1
14	H <sub>2(g)</sub>	0	1,2
15	O2(g)	0	1,2
16	H <sub>2</sub> O <sub>(aq)</sub>	-237.18	1,2

140	Table S1.	Thermodynamic	values (i.e.,	Gibbs free energies)	) for key solids	or aqueous species.
		2			-	1 1

141 The values are taken from various sources.

143	Table S2.	Reactions	and their	equilibrium	constants	for key	aqueous	species i	n the	pipe loc	op
				1		-	1	1		1 1	

system. Constants are taken from various sources. The equilibrium constant for Reaction 16 was

No.	Equilibrium Expressions	Log K	Source
1	$H_2O \rightarrow H^+ + OH^-$	-13.997	1,2
2	$H_2CO_3^* \rightarrow H^+ + HCO_3^-$	-6.352	1,2
3	$HCO_3^- \rightarrow H^+ + CO_3^{2-}$	-10.329	1,2
4	$H_3PO_{4(aq)} \rightarrow H^+ + H_2PO_4^-$	-2.148	2
5	$H_2PO_4^{2-} \rightarrow H^+ + HPO_4^{2-}$	-7.198	2
б	$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$	-12.375	2
7	$Pb^{2+} + H_2O \rightarrow PbOH^+ + H^+$	-7.597	2
8	$PbOH^{+} + H_2O \rightarrow Pb(OH)_{2(aq)} + H^{+}$	-9.497	2
9	$Pb(OH)_{2(aq)} + H_2O \rightarrow Pb(OH)_3^- + H^+$	-10.997	2
10	$Pb(OH)_{3}^{-} + H_2O \rightarrow Pb(OH)_{4}^{2-} + H^+$	-11.608	2
11	$Pb^{2+} + CO_3^{2-} \rightarrow PbCO_{3(aq)}$	6.478	2
12	$Pb^{2+}$ + 2CO <sub>3</sub> <sup>2-</sup> → $Pb(CO_3)_2^{2-}$	9.938	2
13	$Pb^{2+} + HCO_3^- \rightarrow PbHCO_3^+$	13.20	2
14	$PbCO_{3(s)} \rightarrow Pb^{2+} + CO_3^{2-}$	-13.13	2
15	$Pb_{5}(PO_{4})_{3}OH_{(s)} + H^{+} \rightarrow 5Pb^{2+} + 3PO_{4}^{3-} + H_{2}O$	-69.79	2
16	$PbO_{2(s)} + 2H^{+} + Cl^{-} \rightarrow Pb^{2+} + OCl^{-} + 2H_2O$	-8.82	1
17	$HOCl_{(aq)} \rightarrow H^+ + OCl^-$	-7.60	1

145	calculated from molar	Gibbs free	energies of	of each	component	of the reaction.
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#### 147 Section S1. Specific Information about Pipe Loop System.

Six replicates of the assemblies of new pipe with the pipe reactor apparatus were built 148 with new lead pipes: inner diameters of 0.75 inch and outer diameters of 1.0 inch. The small 149 segments enabled convenient characterization of pipe scales after conditioning. Water was 150 circulated by magnetic drive pumps (1-MD, Little Giant, OK). Flow rate was monitored by 151 152 flowmeters (F-400, Blue-White, CA). The pipes and tubing other than the lead sections were composed of polyvinyl chloride (PVC) or flexible plastic. Downstream and upstream valves 153 enabled sampling of the target solution inside the pipe through sampling ports next to the valves. 154 155 To hold the water used for each pipe loop, 11-L carboys (McMaster-Carr) were used. Polyvinyl chloride (PVC, Schedule 40) pipe sections (McMaster-Carr) were cut into 156 several lengths and used for connecting lead pipe segments (Schedule 40, I.D: 1.058 inch, 157 McMaster-Carr) (Figure S3). Segments from each original lead pipe had pieces of 0.75-inch-158 length PVC pipe epoxied (J-B Weld) to their ends. This approach covered the lead surface at the 159 160 end of the pipe that was exposed during cutting, and it provided each segment with a PVC end that could be connected using standard fittings. The segments were then connected using PVC 161 unions, which allowed removal of lead pipe segments during experiments with essentially no 162 163 disturbance (e.g., no cutting) to the remaining lead pipe segments.

Although the use of new lead pipes with an artificial water is not entirely the same as working with decades-old lead pipes either in the field or harvested from the field, this approach offered several advantages for gaining mechanistic insights into the processes governing lead release. First, the pure lead pipe is free of any external metals. Because the starting material is pure unaltered lead, reproducible results could be obtained among six lead pipe reactors. Second, in our synthetic fresh tap water, we can provide a controlled and constant dose of free chlorine

while developing PbO<sub>2(s)</sub>-rich scales. During reduction we do not have the complexity of natural
organic matter and other reductants that may be present in actual water supplies at concentrations
that vary seasonally. Third, we were able to maintain a constant water temperature (i.e., 22 °C),
so that temperature was not a variable and we could focus on the impacts of changing water
chemistry on lead release.

(a)





- **Figure S3.** Photographs of (a) overall pipe reactors and (b) components of each pipe assembly
- 177 with cut lead pipe segments.

Water Composition	Pango for	Synthetic Water		
Parameter	Washington, D.C., Water	Target value	Actual value	
Total Chlorine, mg/L as Cl <sub>2</sub>	2.3-3.8**	1.0-2.0***	1.0-2.0	
рН	7.7-7.8	7.70	7.70	
Total Alkalinity, mg/L as CaCO <sub>3</sub>	49-99	76	73.2	
TDS, mg/L	126-261	208	331****	
Total Hardness, mg/L as CaCO <sub>3</sub>	114-155	141	142.5	
Chloride, mg/L	30-56	34	34	
Sulfate, mg/L	40-71	50	50	
Calcium, mg/L	26-52	42	42.1	
Magnesium, mg/L	3-12	9	9.1	
Sodium, mg/L	15-40	15	37.5	
*Phosphate, mg/L as PO4	1.9-2.8	0 or 3.0	0 or 3.0	
Fluoride, mg/L	0.4-0.8	0.86	0.86	
Nitrate, mg/L	2.7 - 8.9	-	7.61	
Ionic Strength (M) *****	-	-	$6.5  imes 10^{-3}$	

**Table S3.** Composition of synthetic Washington, D.C., tap water.

<sup>179</sup> \* For phosphate, two different concentrations were indicated since three of the six pipe

assemblies are receiving phosphate, while the other three do not receive phosphate.

181 \*\* From Water Quality Report, Washington, D.C., Drinking Water (1999-2000).

182 \*\*\* The target free chlorine concentration was  $1.0 \text{ mg/L } \text{Cl}_2$  for the first 18 weeks. Then, from

Week 19, the target free chlorine concentration was increased to  $2.0 \text{ mg/L Cl}_2$ .

\*\*\*\* The actual TDS values were calculated based the contents of substances added in the
synthetic tap water.

186 \*\*\*\*\* Ionic strength slightly varied depending on the phosphate and free chlorine additions.

## 187 Section S2. Chemical Reagents and Artificial Tap Water Compositions.

188	Chemical Reagents. To simulate pre-2000 Washington, D.C., tap water for the
189	experiments, we used sodium bicarbonate (NaHCO <sub>3</sub> , ≥99.7%, Sigma-Aldrich, Saint Louis, MO),
190	calcium chloride (CaCl <sub>2</sub> ·2H <sub>2</sub> O, 99.0-105%, Alfa-Aesar, MA), calcium sulfate (CaSO <sub>4</sub> , 99%,
191	Acros Organics, NJ), calcium nitrate (Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, 100.0%, Fisher Scientific, Fair Lawn,
192	NJ), sodium fluoride (NaF, (≥99%, Sigma-Aldrich, Saint Louis, MO), sodium hypochlorite
193	(NaOCl, 5.65–6%, Fisher Scientific, Fair Lawn, NJ), ammonium chloride (NH4Cl, 99.7%, Fisher
194	Scientific, Fair Lawn, NJ), nitric acid (HNO <sub>3</sub> , 68.0-70.0%, Alfa-Aesar, MA), and sodium
195	phosphate monobasic (NaH <sub>2</sub> PO <sub>4</sub> , 99%, Fisher Scientific, Fair Lawn, NJ). These chemicals were
196	sufficiently pure for the experiments. All solutions were prepared using ultrapure water with a
197	resistivity higher than 18.2 M $\Omega$ -cm.
198	To measure chlorine and phosphate concentrations by colorimetric methods, the
199	following chemicals were used: DPD reagent (N,N-diethyl-p-phenylene diamine, Alfa-Aesar,
200	MA), ethylenediamine tetracetic acid disodium (Na2EDTA, MP Biomeidcals, LLC, Solon, OH),
201	potassium phosphate (KH₂PO₄, ≥99.0%, Sigma-Aldrich, Saint Louis, MO), ammonium
202	molybdate tetrahydrate ((NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O, 81.5%, Fisher Scientific, Fair Lawn, NJ),
203	antimony potassium tartrate (C <sub>8</sub> H <sub>10</sub> K <sub>2</sub> O <sub>15</sub> Sb <sub>2</sub> , LabChem Inc., Pittsburgh, PA), ascorbic acid
204	(C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> , Sigma-Aldrich, Saint Louis, MO), acetone (C <sub>3</sub> H <sub>6</sub> O, ≥99.9%, Sigma-Aldrich, Saint
205	Louis, MO), sulfuric acid (H <sub>2</sub> SO <sub>4</sub> , 95-98%, Sigma-Aldrich, Saint Louis, MO), sodium bisulfite
206	(NaHSO <sub>3</sub> , $\geq$ 90%, Macron Fine Chemicals, PA) and hydroxylamine hydrochloride (NH <sub>2</sub> OH·HCl,
207	>99%, Acros Organics, NJ).

208	Artificial Tap Water Compositions. In the artificial Washington, D.C., tap water (Table
209	S3), the target alkalinity (mainly dissolved inorganic carbon (DIC) concentration) was provided
210	by adding NaHCO <sub>3</sub> stock solution, and it was occasionally confirmed by titration. For the first 18
211	weeks, the target free chlorine concentration was 1.0 mg/L Cl <sub>2</sub> . Beginning in Week 19, we
212	increased the target free chlorine concentration to $2.0 \text{ mg/L Cl}_2$ in an effort to accelerate the
213	formation of $PbO_{2(s)}$ . Tap water with free chlorine was prepared by adding NaOCl stock solution.
214	To prepare tap water with phosphate for half of the pipe loops beginning in Week 66, aliquots of
215	a NaH <sub>2</sub> PO <sub>4</sub> stock solution were added to provide the desired concentration. For tap water with
216	monochloramine (2.0 mg/L Cl <sub>2</sub> ), which was added to all pipe loops starting in Week 80, NaOCl
217	and NH <sub>4</sub> Cl solutions were mixed to obtain an approximately 0.88 Cl <sub>2</sub> :N molar ratio (4.5:1.0
218	Cl <sub>2</sub> :N mass ratio), which is in the range used in practice. <sup>5,6</sup>

#### 219 Section S3. Sample Collection and Pretreatment.

Samples were collected based on a weekly cycle of the pipe loop operation. The weekly 220 timeline of the pipe experiments is illustrated in Figure S4. Before initiating the flow cycle on 221 222 the first day of the week, 50-mL water samples were collected directly from each carboy (0-h samples). The total volume of the lead pipe parts was calculated to be 0.428 L. We should note 223 224 that the lead pipe assembly includes both the lead pipes themselves (total 90 cm length) and the plastic connections (total 60 cm length). Thus, the volume of water directly contacting the lead 225 pipe surface during stagnation was 0.257 L. After a one-week cycle was finished, all of the water 226 227 remaining in each carboy was treated with hydroxylamine (200 mg/L) and acidified with nitric acid to a final concentration of 1% (w/w). This treatment was performed to dissolve any lead-228 229 containing particles, including PbO<sub>2(s)</sub>, that would have accumulated in the recirculating reservoirs and to desorb any lead that was bound to the reservoir walls. Samples were obtained 230 from these acidified carboys for total lead analysis (168-h samples). 231

Before acidifying the carboys or sample bottles, 10-50 mL aliquots were obtained and
kept in 50 mL tubes. Parts of these aliquots (e.g., approximately 5 mL) were filtered with 0.2-µm
polyethersulfone membrane filter (Tisch Scientific, OH) for measuring the dissolved lead
concentrations. Before ICP-MS measurements, these filtered samples were diluted and adjusted
to 1% nitric acid.

Once 168-h samples were measured, carboys were emptied and rinsed with reverse osmosis water and ultrapure water several times. After the simulated tap water was formulated in these carboys, the lead levels of fresh tap waters (0-h samples) were checked (Section S4). From Weeks 80 to 83, we collected samples daily from each pipe loop in order to investigate how the

241 lead concentrations changed with higher temporal resolution than during other stages of the

242 experiment.

243





#### 248 Section S4. 0-hr Samples: Fresh Tap Water in Carboys

The concentrations of lead in the freshly prepared carboys of synthetic tap water (0-h 249 samples) were measured every week (Figure S5). Ideally there should be no measurable lead in 250 251 the initially prepared water, but there is the potential for some carryover of lead from a previous week because the same carboys are used. The results shown in Figure S5 indicate that the lead 252 concentrations were occasionally higher through week 60, which we thought was due to residual 253 lead remaining after use in a previous week. In order to prevent this, we more carefully cleaned 254 the carboys with deionized water several times and also occasionally pretreated them with 1~2% 255 256 nitric acid to clean the inner surface of the carboys. Consequently, lead concentrations notably decreased, and initial lead concentrations were almost always less than 10 µg/L. After Week 50, 257 there were very few residual lead problems. 258



259

Figure S5. Lead concentrations of synthetic tap water before it flows through the lead pipeassemblies (0-h samples).

#### 262 Section S5. Analysis of Water Samples.

Lead and other element concentrations were analyzed by inductively coupled plasma 263 mass spectrometry (ICP-MS, ELAN DRC II, PerkinElmer). The samples were acidified to a final 264 nitric acid concentration of 1% (w/w) before analysis, enough to thoroughly dissolve lead- and 265 cation-containing particles in the water samples. Especially for total lead measurement, carboys 266 267 or sample bottles with the circulated tap water were entirely reduced with hydroxylamine hydrochloride and held for 24 hours; these containers were then entirely acidified (1%, w/w) and 268 held for approximately 48 hours. Samples for ICP-MS were diluted by a factor of two to lower 269 270 the lead and other cation concentrations to be in the ideal calibration range of the instrument. The detection limit of lead on our ICP-MS instrument was generally 0.1 µg/L or better. In order to 271 accurately quantify the large range of lead concentrations obtained from ICP-MS, both weighted 272 and unweighted regressions were applied to ICP-MS raw data. 273

274 Free chlorine and combined chlorine (i.e., monochloramine) concentrations were 275 measured by the DPD (N,N-diethyl-p-phenylenediamine) method (4500-Cl G, Standard Method) 276 <sup>7</sup> with a UV-Vis spectrophotometer at 515 nm. Phosphate concentrations were measured by the molybdate colorimetric method (Method 365.3, EPA, 1978)<sup>7</sup> with a UV-Vis spectrophotometer 277 278 at 650 nm. For phosphate measurements, we pretreated the samples with sodium bisulfite in order to remove oxidants (i.e., chlorine) before applying the molybdate colorimetric treatment. 279 The solution pH was measured with a pH electrode (Accumet, Fisher Scientific) and pH meter 280 281 (AB150, Fisher Scientific). At the start of the project, in order to confirm the initial DIC concentration, total carbon was analyzed by a total organic carbon analyzer (TOC, TOC-L 282 Series, Shimadzu, Japan). Occasionally, dynamic light scattering (DLS, Malvern Zetasizer) was 283 performed on the simulated tap water to probe for any trends in the average size of suspended 284 particles. 285

At the beginning of each daily cycle, 10-mL samples were collected from each carboy for monitoring chlorine concentration. Based on the measured decrease in the free chlorine concentration, the concentration was adjusted back to the target value (1 or 2 mg/L as Cl<sub>2</sub>) by adding free chlorine stock solution. The value of the pH was measured daily in 50 mL samples contained in 60 mL-polypropylene bottles with gas-tight covers that allowed the entry of a pH electrode without any exchange of the water sample with the atmosphere. When this gas-tight approach was not used, CO<sub>2</sub> exsolution from the water resulted in an upward drift in pH.

#### 293 Section S6. Solid Characterization: Sample Preparation and Analyses

### 294 Analysis of Pipe Scales: Preparation of Materials (Figure S6).

The cuts for preparing the cross-sections were made after one end of a pipe segment was filled with epoxy (145-2005, 20010, Allied High Tech). After the epoxy had hardened, a disk from that end was cut and polished. The remaining pipe section (at least 2-inches) was cut to provide inner-surface-exposing cylinders. In some cases, portions of scale were carefully scraped with a spatula from the pipe surfaces.

300



- **Figure S6.** Approach for preparing pipe samples for analysis and the associated analyses
- 303 performed on cross sections and inner pipe surfaces.

#### 304 Analytical Methods: Solid Characterization.

For Raman analysis, we used a fiber-optically coupled Raman microprobe (HoloLab 305 series 5000 Raman Microprobe, Kaiser Optical System, Inc., MI) with an excitation wavelength 306 of 532 nm and operated at 0.5 mW at the sample surface. The laser was focused by a  $50 \times (N.A.$ 307 = 0.55) or  $80 \times (N.A. = 0.75)$  Olympus objective onto the sample. Most analyses were made in 308 309 situ by focusing 0.5 mW laser power into a beam of  $1-2 \,\mu\text{m}$  diameter directly onto the inner surface of the pipe bore. Such a low laser power was chosen to avoid destructive heating and/or 310 oxidation of these mostly opaque scales. Through this approach, the identity, stability and 311 312 crystallinity of the scales were preserved. It was therefore possible to record and interpret differences in phases and in the degree of crystallinity among the samples. 313 X-ray diffraction (XRD) was used to identify crystalline phases of scale powders scraped 314 from the inner surface of the lead pipe segments. A Bruker d8 Advance X-ray diffractometer 315 (Bruker, MA) equipped with a LynxEyeXE detector and Cu x-ray tube was used. Voltage and 316 current values were 40 kV and 40 mA, respectively, with  $0.02^{\circ} 2\theta$  step size and the sample 317 holder rotating at 15 rotations per minute. The scanning range was  $5-80^{\circ} 2\theta$ . 318 Polished cross sections of the pipe segments were viewed with scanning electron 319 320 microscopy (SEM, A JEOL 7001LVF Field Emission, JEOL, Japan) with elemental analysis information provided by energy-dispersive X-ray spectroscopy (EDS). The EDS results were 321 322 obtained from points near the inner surface of the lead pipe in order to analyze the composition 323 of the scale; unaltered lead pipe has a signal only from lead. SEM-EDS images of lead pipe cross-section disks were produced by either secondary electrons or back-scattered electrons. 324 325 Note that, for both imaging and EDS analysis, the samples were analyzed uncoated. For 326 elemental mapping, the M $\alpha$  line was used for Pb instead of the L $\alpha$  or K $\alpha$  line since analyses were

- performed with a beam energy lower than 10 keV. For other elements (e.g., Mn, Ca, and P), the
- 328 K $\alpha$  lines were used. Compositional information was obtained and expressed as the relative (%)
- atomic portions of each element. Optical images were taken of the half cylinders of pipe
- segments with a 12MP camera of an iPhone7 (Apple Inc., CA).

#### Section S7. Conditioning Lead Pipe Assemblies for First 50 Weeks

In order to make a  $PbO_{2(s)}$  scale similar to what was on lead service lines in Washington, D.C., before November 2000, the lead pipe assemblies were conditioned with pre-2000 artificial Washington, D.C., tap water (Table S3). The results that we obtained during the first 50 weeks of conditioning are important for convincing ourselves that the lead pipe assemblies had formed stable  $PbO_{2(s)}$  scale. In the following sections, we describe the lead concentrations, water chemistry, and solid characterization (i.e., SEM images and Raman spectra) during the first 50 weeks of conditioning.

339

#### 340 Section S7-1. Lead Concentrations during the Conditioning Period (0-50 weeks)

Total Pb concentrations for the first week were higher than 200  $\mu$ g/L (Figure S7a). The 341 total Pb concentrations dropped significantly after the first week and then gradually decreased 342 further. Starting in Week 10, the concentrations from the six pipe assemblies converged at 343 around 75  $\mu$ g/L. After Week 8, we also started to measure the dissolved lead concentration in the 344 recirculating reservoir. The dissolved lead concentrations were close to but slightly lower than 345 the total lead concentrations, with values around the predicted solubility of cerussite (i.e., 68 346  $\mu$ g/L) (Figure S8). Based on the thermodynamic constants of lead carbonate aqueous 347 complexes,<sup>2,4</sup> lead hydroxide aqueous complexes,<sup>2,4</sup> and cerussite solubility product,<sup>2,4</sup> the 348 equilibrium solubility was calculated for the specific pH and DIC of the water. 349 350 The accidental addition of MnSO<sub>4</sub> instead of MgSO<sub>4</sub> for one day in Week 33 changed the trend of the lead profile. While the total Pb concentration from all six loops was variable for the 351 weeks immediately after this incident, the dissolved Pb concentrations dropped to less than 5 352

 $\mu g/L$ . The noise in the Pb concentrations of the early period after Mn addition (Weeks 33-50)

354 indicated that a significant amount of lead existed in particulate form. As time elapsed, the lead concentrations became more stable. For example, the total lead concentrations for Week 39 were 355  $4.4\pm10.9 \ \mu g/L$ , which were much lower than the values in Week 33 (134.4\pm93.9 \ \mu g/L) prior to 356 357 the one day of Mn addition. The dissolved lead level before Week 33 corresponds to the solubility of cerussite in the Washington, D.C., tap water conditions, suggesting that the inner 358 surfaces of the lead pipes before Week 33 were mainly covered with cerussite. 359 The dissolved lead concentration decreased to below 5  $\mu$ g/L in the 168-h samples after 360 the manganese addition. This decrease could be associated with catalyzed formation of  $PbO_{2(s)}$ , 361 which is less soluble than cerussite. A recent study reported that free chlorine can accelerate 362 oxidation of Pb(II) species to  $PbO_{2(s)}$  when manganese oxide (MnO<sub>2(s)</sub>) is present.<sup>8</sup> 363







372 concentration was determined by ICP-MS by measuring P.



Figure S8. Dissolved lead concentrations from 168-hour carboy samples during lead pipe system 375 conditioning. In Week 33, there was one day in which manganese, instead of magnesium, was 376 added to the synthetic tap water.

378

#### 379 Section S7-2. Water Chemistry during the Conditioning Period.

Chlorine was consumed because free chlorine reacted with the Pb<sup>0</sup> or Pb(II) in the lead 380 pipe (Figure S7). After starting the conditioning, the daily consumption gradually declined until 381 Week 6, and then the extent of free chlorine daily consumption remained stable (i.e., about 20%) 382 until Week 33. We note that during this period, the free chlorine was not measured or readjusted 383 384 during weekends. Over the weekends, the free chlorine dropped from 1 mg/L to approximately 0.65 mg/L during the first 18 weeks. When the target free chlorine was increased to 2 mg/L at 385 the start of Week 19, it dropped from 2 mg/L to approximately 1.2 mg/L over the following 386 387 weekends. Free chlorine consumption during the weekends is not shown in Figure 2b. The values in free chlorine concentrations greater than 2 mg/L that are occasionally seen in Figure 2b 388 389 happened because our estimated amounts of free chlorine stock solution needed for adjustment were sometimes too high. 390

In Week 33 (*Stage 2*), MnSO<sub>4</sub> was mistakenly added to all the pipe reactors, and daily 391 392 free chlorine consumption increased substantially after this addition. From Weeks 33 to Week 39, the free chlorine concentration dropped to below 0.5 mg/L within a day. This period of 393 greater chlorine consumption is consistent with the lead concentration data that indicate that this 394 395 was a period of extensive formation of  $PbO_{2(s)}$ . The greater chlorine consumption here could be associated with the greater extent of oxidation of Pb(II) species to PbO<sub>2(s)</sub> and of elemental lead 396 397 to Pb(II) species. After Week 39, the free chlorine consumption rate gradually declined. From 398 Week 50 until Week 80, 70-80% residual free chlorine remained after one-day recirculation. Our criteria for moving to the main experimental test phase were 1) an average daily chlorine 399 400 consumption of less than 0.6 mg/L/day and 2) a total lead concentration below  $5 \mu g/L$ .

Through the course of each week of recirculation, the pH increased from an initial value of 7.7 to about 8.1-8.3 (Figure 2c). For both free chlorine concentrations and the pH, the six new lead pipe assemblies all behaved similarly. The pH of the pipe assemblies at the end of each week was practically constant through 60 weeks of conditioning, suggesting that pH was not affected by whether pipe scales were dominated by cerussite or lead(IV) oxide.

406

#### 407 Section S7-3. Scale Analysis: Scanning Electron Microscopy at Weeks 15 and 35

The surface color of the in-situ pipe scale gradually transformed from dark gray to dark 408 409 red (Figure S9). Optical images of the half cylinder's inner surfaces were compared for pipe sections conditioned for different times. Week 15 pipe scale shows a mixture of dark gray and 410 white products. Reddish products were mainly observed on the surface of the Week 35 sample. 411 Based on the dissolved lead concentrations presented in the previous section, the reddish-color 412 might be scrutinyite ( $\alpha$ -PbO<sub>2(s)</sub>) or plattnerite ( $\beta$ -PbO<sub>2(s)</sub>), both of which can exhibit that color. 413 The Week 15 pipe segment has an extremely thin scale ( $<1 \mu m$ ). The scale on the Week 35 pipe 414 section is 2-3 µm thick. The scale contains substantial amounts of oxygen and manganese, 415 suggesting that it is probably a mixture of lead corrosion products and manganese oxide. The 416 417 scale thickness difference between Weeks 15 and 35 suggests that even though PbO<sub>2(s)</sub> was mainly observed after Week 35, the quantity of corrosion product gradually increased throughout 418 419 the elapsed time.



- 422 **Figure S9.** Optical images taken from the half cylinder's inner surface (upper), and scanning
- 423 electron micrographs from cross-section disk (lower): (a) Week 15 and (b) Week 35.



Figure S10. Raman spectra of pipe scale on new lead pipe from (a) Week 15 and (b) Week 35.
Peaks corresponding to particular phases are noted. In panel b, multiple peaks are recorded from
various spots on surface of each half-cylinder. Each 'White-yellow fluffy phases', 'Bright white
with fine blades', 'Mixture of red and gray', and 'Raised red area' is indicated on the picture of
Figure S11.

# Week 35



430

**Figure S11.** Optical images taken from the locations where Raman spectra were obtained on the

432 inner surface of a pipe segment from Week 35.

#### 433 Section S7-4. Results from Raman Spectroscopy: Weeks 15 and 35

Raman microprobe analyses were carried out in situ on the thin scales that had developed 434 on the inside pipe walls during 15 weeks of conditioning by synthetic water during its free-435 chlorine disinfection period (Figure S10a). Low-magnification observation with a binocular 436 microscope reveals a mostly homogeneous, dark gray matte surface that is suggestive of coating 437 438 by a very fine-grained material. Small (millimeter-scale) light-gray, highly reflecting patches suggest that the underlying lead pipe is still uncoated in places. Higher magnification under 439 reflected-light microscopy reveals brownish circles, hundreds of micrometers in diameter, 440 441 apparently superimposed on the dominant gray surface. Red features/grains on the scale of several micrometers are dispersed throughout the gray matrix. Raman spectroscopy and 442 accompanying optical microscopy show the dark gray coating phase to be litharge, with a 443 spectrum directly matching that in the literature. This coating must be very thin and perhaps not 444 totally continuous, i.e., on the order of micrometers, because the spectral bands of cerussite are 445 446 present in all the spectra of the gray coating (Figure S10a). Clearly, cerussite consistently underlies the gray coating. Occasionally, the spectrum with litharge bands has an additional 447 weak band at about 225 cm<sup>-1</sup>, suggestive of  $\alpha$ -PbO<sub>2(s)</sub>. The brightly reflecting light gray areas 448 449 were found to be elemental lead coated by colorless, transparent cerussite (major scale phase), which in turn is coated by litharge so thin that its color/presence is not recognized optically. The 450 451 brownish rings spectrally reveal a dominance of cerussite over litharge, suggesting that the 452 litharge coating is thinner in these places.

453 Raman spectroscopy of the Week 35 segment shows the reddish coating phase to be 454 mainly  $\alpha$ -PbO<sub>2(s)</sub> and  $\beta$ -PbO<sub>2(s)</sub> (Figure S10b). Provisional identifications were made by 455 comparison to Raman spectra of Pb phases in the literature: spectra with a band at about 600 cm<sup>-</sup>

- 456 <sup>1</sup> and 635 cm<sup>-1</sup> match with  $\alpha$ -PbO<sub>2(s)</sub> and  $\beta$ -PbO<sub>2(s)</sub>, respectively. Additionally, white-yellow
- 457 fluffy phases reside on some of the reddish area (Figure S11). These fluffy phases are best
- 458 correlated with a band at about 1055 cm<sup>-1</sup>, which is diagnostic for lead carbonate (i.e., mixture of
- 459 cerussite and hydrocerussite). In the Week 15 segment, cerussite consistently underlies a gray
- 460 coating that in some places was identified spectroscopically as litharge.

461 Section S8. Lead Concentrations of 8-hr Samples (Lead Pipe Segment Stagnation Samples).

The lead concentrations of these 8-h samples for the initial three weeks were very high, in the range of 94 to 4,000  $\mu$ g/L (Figure S9). We then continued conditioning the lead pipes without collecting the 8-h samples until Week 8. Once measurements commenced again at Week 8, the lead concentrations were stable at around 70  $\mu$ g/L, until Week 32, and both total and dissolved lead concentrations were 60-70  $\mu$ g/L, similar to the 168-h samples.

The one-time inadvertent addition of MnSO<sub>4</sub> in Week 33 strongly influenced the lead 467 concentrations. For 8-h samples, both dissolved and total lead concentrations increased and 468 469 became variable for a few weeks (Figure S9 and S10). The total lead concentration was much higher than the dissolved lead concentration for most samples, suggesting that particulate lead 470 471 became dominant after the manganese addition. Between Weeks 33 and 50, the range of total lead concentrations of 8-h samples went up to 920  $\mu$ g/L. The variations of total lead 472 concentrations for 8-h samples were higher than those of 168-h samples. The average lead 473 474 concentration of 8-h samples during this period was 170.9  $\mu$ g/L, while that of the 168-h samples was 54  $\mu$ g/L. Between Weeks 33 and 45, the overall dissolved lead concentrations in 8-h 475 samples were higher than those in 168-h samples. The average dissolved lead concentrations in 476 477 8-h samples was 27.4  $\mu$ g/L, while that in 168-h samples was 5.1  $\mu$ g/L.

From Weeks 32 to 50, the higher dissolved lead concentrations in 8-h samples offers two possibilities. First, the rate of lead dissolution from  $PbCO_{3(s)}$  or  $Pb^{0}$  was faster than the rate of lead fixation (e.g., precipitation as  $PbO_{2(s)}$  or adsorption on  $PbO_{2(s)}$ ). Here, we need to assume that  $PbO_{2(s)}$  formation by Mn introduction occurred by simultaneous reaction of dissolution of pre-existing lead compound (e.g., bare lead or lead carbonate) and fixation of dissolved lead to  $PbO_{2(s)}$ . A second possibility is that  $PbO_{2(s)}$  was initial formed as fine particles (i.e., diameter

smaller than the 0.2 µm pore size of the filters), and then became larger, probably by reaction
between dissolved lead and particulate PbO<sub>2(s)</sub>, or by aggregation.

The average total and dissolved lead concentrations dropped below 50  $\mu$ g/L after Week 50 and 40, respectively. Even after Week 50, several outliers (i.e., Pb levels higher than 50  $\mu$ g/L) were formed for total lead concentrations. However, dissolved lead concentrations remained below 5  $\mu$ g/L.

With orthophosphate addition, the average total lead concentration in 8-h samples from 490 Weeks 81-90 was 10.7 µg/L, while that in 168-h samples was 12.3 µg/L (Table S1). With 491 492 orthophosphate, average total lead concentration in 8-h samples from Weeks 91-95 was 7.7  $\mu$ g/L, while that in 168-h is 12.7  $\mu$ g/L. Without orthophosphate, the average total lead 493 concentration in 8-h samples from Weeks 81-90 was 118.5 µg/L, while that in 168-h samples 494 was 117.8  $\mu$ g/L. Without orthophosphate, the average total lead concentration in 8-h samples 495 from Weeks 91-95 was 87.5 µg/L, while that in 168-h was 108.8 µg/L. With PO<sub>4</sub> condition, 496 497 dissolved Pb concentrations of 8-h and 168-h samples showed similar tendency (even slightly lower). 498

A few outliers in the total lead concentrations in the 8-h samples after Week 50 suggest 499 500 that particles occasionally detached from the pipes. These outliers were only seen in the 8-h samples and not in the 168-h samples. There are three possible reasons for the appearance of 501 502 particulate lead in 8-h samples and not 168-h samples. First, particulate lead may have been 503 released only in the initial period of each week after fresh water was introduced. The resulting water with high particulate Pb concentration would then have been diluted with all of the water 504 505 in the system by the time the 168-h samples were collected. Second, a substantial amount of 506 particulate Pb may have remained in the pipe sections, without moving to other regions of the

507 loops during recirculation. Third, particulate lead formed in the water in the 8-h samples may

508 have deposited on the lead pipe surface during the week-long recirculation so that it was no

509 longer suspended in the 168-h samples.

510

511

Table S4. Comparing total lead concentrations after disinfectant switch. Here, the concentrationvalues are the average of three pipe loops for each condition.

(µg/L)	With Pł	nosphate	Without Phosphate		
	81-90 w	91-95 w	81-90 w	91-95 w	
8-h	10.7	7.7	118.5	87.5	
168-h	12.3	12.7	117.8	108.8	



514

Figure S12. Profiles of pipe loops from solutions kept in pipe parts stagnant for 8 hours (8-h
samples): (a) total lead concentration, (b) chlorine concentration, (c) pH, and (d) orthophosphate
concentration. Experimental details are identical with 168-h samples which were indicated in
Fig. 3.



519

Figure S13. Dissolved lead concentrations of the water after 8 hours of stagnation in the lead
pipe assembly. Dissolved lead concentrations were measured starting in Week 15. In Week 33,
there was one day in which manganese instead of magnesium was added to the synthetic tap
water.



524

525

Figure S14. Total (a) and dissolved lead concentrations (b) from samples taken from pipe loops
during the weekly recirculation. Here, the carboys were exchanged with fresh ones at the end of
each week.

#### 529 Section S9. The pH Increase Associated with Lead Oxidation

The pH change during the conditioning and main experiment was probably due to the competing reactions of hydrogen ion (H<sup>+</sup>) consumption by the oxidation of Pb<sup>0</sup> to Pb(II) species and H<sup>+</sup> production by the oxidation of Pb(II) species to PbO<sub>2(s)</sub>:

533

534 
$$Pb^{0} + OCl^{-} + HCO_{3}^{-} + H^{+} \rightarrow PbCO_{3(aq)} + Cl^{-} + H_{2}O$$
 (eq S9-1)

535 
$$PbCO_{3(aq)} + OCl^{-} + H_2O \rightarrow PbO_{2(s)} + HCO_3^{-} + Cl^{-} + H^{+}$$
 (eq S9-2)

536

537 For Pb(II) species, PbCO<sub>3(aq)</sub> was focused on because it is the dominant dissolved lead species

under conditions of pH 7.7 with DIC 1.57 mM. Other cerussite-related reactions were not

539 presented because those formulations are similar to those in the above equations.

The pH increase suggests that  $Pb^0$  oxidation to Pb(II) species were dominant even after PbO<sub>2(s)</sub> was formed. It is still unknown why the pH increased even after  $PbO_{2(s)}$  had substantially formed. The pH increase was less when phosphate was present, because phosphate has acid-base chemistry that allows it to contribute some pH buffering.

544 We speculate that the retardation in pH increase in Loops 1-3 after Week 80 (Figure 2c)

545 was not related with Pb(II) species transforming to P-containing solids (e.g.,

546 hydroxylpyromorphite). We considered the following three reactions.

547

548
$$Pb^{2+} + 3HPO_4^{2-} + H_2O \rightarrow Pb_5(PO_4)_3OH_{(s)} + 4H^+$$
(eq 9-3)549 $PbOH^+ + 3HPO_4^{2-} + H^+ \rightarrow Pb_5(PO_4)_3OH_{(s)} + 4H_2O$ (eq 9-4)550 $PbCO_{3(aq)} + 3HPO_4^{2-} + H_2O + H^+ \rightarrow Pb_5(PO_4)_3OH_{(s)} + HCO_3^-$ (eq 9-5)

551 Since concentrations of PbOH<sup>+</sup> and PbCO<sub>3(aq)</sub> were higher than that of  $Pb^{2+}$  in our tap water, we

- believe equations 2 and 3 are dominant rather than equation 1, suggesting that formation of
- 553 phosphate-containing solids might promote pH increase. It is speculated that factors other than
- the formation of phosphate-containing solids retarded the increase in pH of Loops 1-3.

#### 555 Section S10. Amounts of Phosphorus Deposited in the Scales.

Based on the phosphorus concentrations of Loop 2 from Weeks 66 to 72 (Figure S13), the amount of phosphorus deposited on the inner surfaces of lead pipe or lead pipe reactors was calculated. Specifically, in order to calculate the mass of phosphorus deposited, the difference between initial and 168-h phosphorus concentrations were multiplied by the volume of tap water (i.e., 10 liter). The calculation shows that approximately 8.8 mg of phosphorus was accumulated on the inner surfaces of lead pipe or lead pipe reactors of Loop 2.

By assuming that the thickness and surface area of scale are 10  $\mu$ m and 255 cm<sup>2</sup>, respectively, the scale volume would be 0.255 cm<sup>3</sup>. The scale mass is estimated as 2.39 g by multiplying the scale density by the scale volume: here, we will assume the density of scale is identical to that of PbO<sub>2(s)</sub> (i.e., 9.38 g/cm<sup>3</sup>).

Finally, the phosphorus portion of the scale is calculated to be approximately 0.3% (w/w). This value is close to the detection limit of SEM-EDS, so it is not surprising that it was not clearly observed by SEM-EDS (0.0-0.1%, w/w) in the scale of the pipe segment collected in Week 72.

570 By using the same process, the amounts of phosphorus in the scales of pipe segments 571 collected in Weeks 83 and 95 were calculated to be 0.3% and 3.2% (atomic percentage), 572 respectively. The trends in these values are consistent with the semi-quantitative analysis by 573 SEM-EDS (Figure S20).



575

Figure S15. Total and dissolved phosphate concentrations of Loops 1, 2, and 3 for the samples 576 collected at the end of each week. The thick green line indicates the average total phosphate 577 578 concentrations from freshly prepared carboys (0-hr samples). Phosphate was added starting in 579 Week 66 (indicated by red dotted line). In Week 80, the disinfectant for all six assemblies was switched from free chlorine to monochloramine (indicated by vertical purple dashed line). The 580 581 phosphate concentration was determined using ICP-MS by measuring P. The phosphate consumption tendency was widely varied among the loops. Before Week 80, Loop 2 showed 582 583 much higher phosphate consumption than Loops 1 and 3. After Week 80, Loop 1 showed higher consumption than the other two. 584



**Figure S16**. Visual images from the surface of the pipe segment from Week 95-1D (with

588 phosphate) (upper) and Week 95-6D (without phosphate) (lower).

#### 589 Section S11. Mineralogical Scale Characterization

#### 590 Section S11-1. Before the Disinfectant Switch: Weeks 62 and 72.

The Raman peaks from the 15-µm corrosion product in Week 62 show that the pipe 591 coating was mainly  $\beta$ -PbO<sub>2(s)</sub> (Figure 5a). Specifically, two different degrees of crystallinity of  $\beta$ -592 PbO<sub>2(s)</sub> were observed. Viewed with an optical microscope (figure not included), reddish  $\beta$ -593  $PbO_{2(s)}$  had two main components: 1) very fine-grained materials at the base of the mineral 594 coating ("matrix"), and 2) small grains on the tips of rod-shaped structures that projected above 595 the matrix (like a "crown"). The matrix was found to be more crystalline  $\beta$ -PbO<sub>2(s)</sub>, while the tips 596 597 of crown were a more poorly ordered form of  $\beta$ -PbO<sub>2(s)</sub>. As early as Week 35 in the overall experiment, multiple broad spectral bands were present that indicated the formation of poorly 598 crystalline oxide phases (Figure S10). These results support an increase in the degree of  $\beta$ -PbO<sub>2(s)</sub> 599 crystallinity during the conditioning process. XRD patterns of the scale powder taken from the 600 Week 62 pipe segment show  $\beta$ -PbO<sub>2(s)</sub> peaks with high intensity and  $\alpha$ -PbO<sub>2(s)</sub> peaks of relatively 601 low intensity (Figure S15a). Like Week 62, the Raman spectra from Week 72 (Figure 5a) had 602 main peaks at around 380 and 520 cm<sup>-1</sup>, representing the PbO<sub>2(s)</sub>. XRD patterns of Week 72 were 603 similar to those of Week 62 (Figure S15b): most of the peaks were characteristic of  $\beta$ -PbO<sub>2(s)</sub> and 604 605  $\alpha$ -PbO<sub>2(s)</sub>. Unaltered lead measured by XRD peaks in both Weeks 62 and 72 came from pieces of bare lead removed from the pipe during the removal of scale from the pipe surface for XRD 606 607 analysis. The similarity in spectra between Weeks 62 and 72 suggests that phosphate did not 608 significantly impact PbO<sub>2(s)</sub> scale as long as free chlorine was present.





610

**Figure S17**. X-ray diffraction patterns of scale scrapings from a pipe at (a) Weeks 62 (without

- 612 phosphate), (b) 72 (with phosphate), (c) 83 (without phosphate), and (b) 83 (with phosphate).
- 613 Here, P is  $\beta$ -PbO<sub>2(s)</sub>, S is  $\alpha$ -PbO<sub>2(s)</sub>, C is cerussite, and Pb<sup>0</sup> is unaltered lead. Panels (c) and (d) are
- on the next page.



**Figure S17**. (Continued from front page)

#### 617 Section S11-2. After the Disinfectant Switch: Week 83.

The XRD patterns of samples from Week 83 with phosphate pre-addition were dominated by PbO<sub>2(s)</sub> (i.e., dominantly  $\beta$ -PbO<sub>2(s)</sub> with trace amount of  $\alpha$ -PbO<sub>2(s)</sub>) while PbO<sub>2(s)</sub> and cerussite were both observed from the scraped powder in the scale of the pipe that had not received phosphate (Figure S15c,d). Also, Raman spectral results at Week 83 (Figure 5) show that PbO<sub>2(s)</sub> was still present in the scale at all the selected locations of the pipe surface from the loop with phosphate pre-addition, while PbO<sub>2(s)</sub> was not detected in most of the spots from the non-phosphate condition (Figure 5c,d).

625

#### 626 Section S11-3. After the Disinfectant Switch: Week 95.

After the disinfectant switch, the Raman spectra and XRD patterns showed clear 627 differences depending on the presence or absence of phosphate. In a pipe without phosphate, a 628 mixture of  $PbCO_{3(s)}$  and litharge ( $PbO_{(s)}$ ) with no  $PbO_{2(s)}$  was detected using Raman 629 spectroscopy only 3 weeks after switching disinfectant (Figure 5c). At 12 weeks afterward (i.e., 630 Week 95), lead carbonate (1055 cm<sup>-1</sup>) was detected (Figure 5e), occasionally accompanied by a 631 very weak OH band (~ 3240 cm<sup>-1</sup>), in the absence of phosphate. XRD patterns of powder 632 633 obtained at the same week without phosphate show that the sharp peaks of cerussite were dominant with a few low-intensity peaks for  $\beta$ -PbO<sub>2(s)</sub> (Figure S16), which suggests that 634 635 crystalline cerussite from its original early precipitation remained or reformed in the scale while 636  $\beta$ -PbO<sub>2(s)</sub> in the scale was dissolving after the disinfectant switch without phosphate. In the presence of phosphate at Week 83, the pipe showed  $\beta$ -PbO<sub>2(s)</sub> (Figure 5d). At Week 637 95, in the presence of phosphate, the trace amount of mixtures of PbO<sub>2(s)</sub> (i.e.,  $\beta$ -PbO<sub>2(s)</sub> and  $\alpha$ -638

 $PbO_{2(s)}$ ) and minium ( $Pb_3O_{4(s)}$ ) were detected on the surface. The Raman spectral results show

640 that  $\beta$ -PbO<sub>2(s)</sub> is relatively common, occurring both alone and in the same spectrum with  $\alpha$ -641 PbO<sub>2(s)</sub>, which were also detected from spectral results from XRD analysis (Figure S17). In 642 addition, abundant steep spectral ramps with drop offs at ~660 cm<sup>-1</sup> indicate that unidentified 643 oxide phases might also be present in the scale.

Scale from Week 95 with phosphate was characterized by two clear Raman peaks at ~945 644 and 980 and a weaker peak at ~1075 cm<sup>-1</sup>, indicative of a phosphate phase. The phosphate spectra 645 were weak, possibly indicating a thin coating. The phosphate phase has an apatite-like spectral 646 pattern. Even though not definitely matching a known phase, these spectra resemble those of the 647 648 mixed Ca-Pb phase phosphohedyphane  $(Ca_2Pb_3(PO_4)_3(Cl,F,OH)_{(s)})$  more than calcium apatite  $(Ca_5(PO_4)_3(Cl,F,OH)_{(s)})$  or pyromorphite  $(Pb_5(PO_4)_3(Cl,F,OH)_{(s)})$ . In addition, a specific spectral 649 feature, apparently of an oxide phase, is associated with the phosphate phase. Neither 650 651 hydroxylpyromorphite, chloropyromorphite, nor any other lead phosphate  $(Pb_3(PO_4)_{2(s)})$  $Pb_9(PO_4)_{6(s)}$ ) was detected in the scale, although such phases had been identified in pipe scales in 652 previous studies.<sup>9,10</sup>. Of significance is that lead-containing phosphate solids were 653 spectroscopically apparent in the scales of the Week 95 pipe but not in the spectra of the scales 654 of the Week 83 pipe. 655

In the scale of the pipe collected in Week 95 with phosphate addition, diverse products without phosphorus also appeared in the spectra. The "ramps" that drop off at 549 and 662 cm<sup>-1</sup> indicate possible unidentified oxide phases. In addition, Raman results occasionally show PbO<sub>(s)</sub>, hydrocerussite, and rare amounts of calcite. As we observed, previous studies also reported that diverse corrosion products coexist in actual pipe scales <sup>11</sup>.



**Figure S18**. X-ray diffraction patterns of scale scrapings from a pipe without phosphate at week 95 (95w-6D). Here, C is cerussite, and P is  $\beta$ -PbO<sub>2(s)</sub>.





Figure S19. X-ray diffraction patterns of scale scrapings from a pipe with phosphate at week 95 666 (95w, Loop 1): (a) outer scale, and (b) inner scale. 667



669

**Figure S20**. Total Ca concentrations of 168-h samples. The blue dotted line indicates the initial

671 Ca concentration of freshly prepared synthetic tap water.

10 μm 10-15	to im
Putre	Pure 6-12 µm
Scale	
Area1	Reale Scale
Ероху	Epoxy

Week 62 (without phosphate)			Week 72 (with phosphate)		
Element	Atomic %		Flowert	Atomic %	
	Area1	Area2	Element	Area3	Area4
СК	82.2	83.9	СК	80.3	67.5
ок	15.5	14.1	ОК	18.4	24.8
Pb M	1.9	1.7	Pb M	0.8	7.2
Mn K	0.4	0.3	Mn K	0.4	0.3
РK	N.D.	N.D.	ΡK	N.D.	0.1

Figure S21. Results of energy dispersive X-ray spectroscopic analysis of inner surface of lead
pipe segment at Week 72. Compositional information within the indicated square or rectangle
regions in the SEM figures was obtained and expressed as the relative (%) atomic proportion of
each element. SEM images were taken from two different spots of cross-section of the pipe scale
in order to provide sufficient compositional information of the scale.

	10 µm 5 µm		10 µm	To to the second s		10-15 μm		
Week 83			Week 95					
without phosphate		with phosphate		without phosphate		with phosphate		
Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %	
Pb M	4.2	Pb M	2.4	Pb M	3.2	Pb M	3.3	

ΡK

CaK

CIK

FΚ

N.D.

0.1

N.D.

N.D.

ΡK

Ca K

CIK

FΚ

3.2

3.0

0.3

0.4

678

**Figure S22.** Results of energy dispersive X-ray spectroscopic analysis of inner surface of lead

680 pipe segment of Weeks 83 and 95. Compositional information within the indicated square or

0.3

0.3

0.1

N.D.

rectangle regions in the SEM figures was obtained and expressed as the relative (%) atomic

682 proportion of each element.

ΡK

CaK

CIK

FΚ

N.D.

0.1

2.9

N.D.

ΡK

CaK

CIK

FK

#### 683 Section S12. Composition of Outer and Inner Layer of Scale from Week 95-1D.

Powder XRD enabled identification of crystalline compounds of each outer and inner layer of Week 95-1D pipe scale (Figure S17). XRD patterns from the powder scraped from the outer scale had peaks matching to patterns of phosphohedyphane-F. The breadth of the peaks of phosphohedyphane-F indicate that the size of its crystallites might be small. In the outer scale, peaks for lead(IV) oxides (i.e.,  $\alpha$ -PbO<sub>2(s)</sub> and  $\beta$ -PbO<sub>2(s)</sub>) and Pb<sup>0</sup> were also seen. Trace amounts of inner scale or unaltered Pb might be mixed while collecting the outer scale powder from the lead pipe segment.

According to the patterns of XRD, the inner scale was mainly composed of  $\alpha$ -PbO<sub>2(s)</sub> and  $\beta$ -PbO<sub>2(s)</sub> (Figure S17b). Their peaks were short and broad, indicating small crystallites. Litharge was also present. During the inner scale scraping, a few particles of unaltered lead were unintentionally collected. Unlike the outer scale, no peaks of Ca- or P-containing solids were observed in the XRD patterns.



Flomont	Atomic %					
Liement	Area1	Area2	Area3	Area4		
Pb Mα	27.8%	19.7%	3.3%	1.8%		
Ο Κα	27.4%	39.2%	21.7%	15.8%		
Ο Κα	44.4%	40.4%	67.0%	76.6%		
Ρ Κα	0.0%	0.2%	3.2%	1.8%		
Ca Kα	0.0%	0.1%	3.0%	1.7%		
F Kα	0.0%	0.0%	0.4%	0.2%		

Figure S23. Results of energy dispersive X-ray spectroscopic analysis of inner surface of Week
(with phosphate) lead pipe segment. Composition information within the indicated red square
regions in the SEM figures was obtained and expressed as the relative (%) atomic proportion of
each element.



**Figure S24**. Mapping image (SEM/EDS) from the surface of the pipe segment from Week 95-

703 6D (without phosphate).

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