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Aggregation of Lead Phosphate Particles: Implication for Lead Removal in Tap Water

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Elevated lead in tap water

Lead (Pb):

- Poses risk to human health
- Sources: lead pipes, scales, joints, etc.
- Action level: 15 $\mu\text{g}/\text{L}$ (Lead and Copper Rule)



Source: flintwaterstudy.org

Occurrences of elevated lead levels in tap water are common nationwide.

- From 2001 to 2004, due to the switch of water disinfectants, high lead concentrations were observed in Washington DC tap water.
- During the recent water crisis in Flint, MI (started in April 2014), lead concentrations over 5,000 $\mu\text{g}/\text{L}$ were detected in tap water.
- Newark, NJ, has been exceeded action level for lead since 2017.
- Last year (2018), elevated lead was found in drinking water at schools across Virginia.

Lead removal

Point of use (POU) devices:

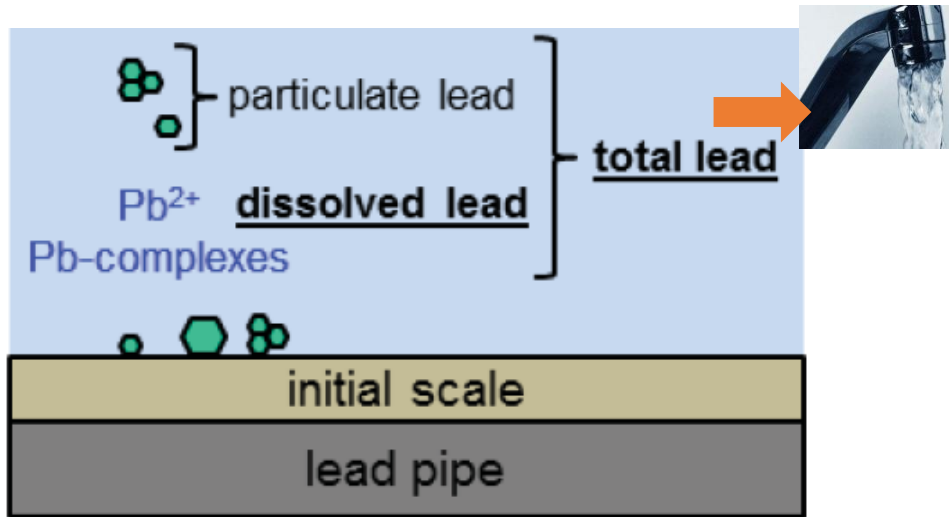
- Ion exchange, adsorption, and membrane filtration
- Not approved approaches to meet a regulation

Corrosion inhibitors: Phosphate, silicate

- **Phosphate is commonly used due to formation of lead phosphate with low solubility**
- However, during the water crisis in Flint, total lead concentration stayed high for months after phosphate addition. Bench-scale pipe studies showed similar observation.



Particulate lead transport and aggregation



Hypothesis:

- Particulate lead phosphate can transport along the distribution pipes and get to tap water.
- Aggregation of lead phosphate particles can affect their transport in pipes, and the aggregation process is influenced by various aqueous parameters.

Objectives:

- Study effects of water chemistry (e.g., PO₄/Pb ratios, ionic strength (IS), cations/anions, natural organic matter (NOM), and pH) on lead phosphate aggregation.
- Explore the controlling mechanisms

Experimental

Solution conditions

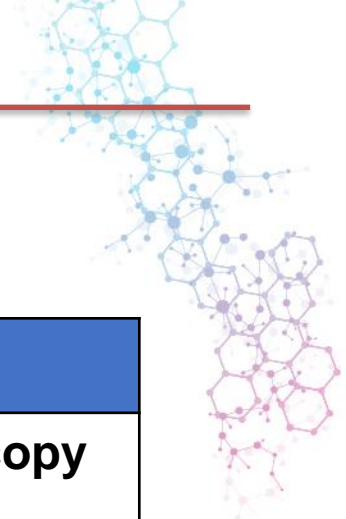
Parameters	Variable	Saturation index (SI) ^b
PO ₄ /Pb ratios	PO ₄ /Pb ratios = 1000, 100, 60, 10, 1 ^a	12.6
Ionic strength (IS) ^a	IS = 0.58, 4, 11, 21, 30, 50, 80, 99 mM ^b	
Cations/Anions	Ca ²⁺ , Mg ²⁺ , Cl ⁻ , F ⁻ , HCO ₃ ^{-a}	
Natural organic matters (NOM)	NOM (0.05 - 5 mg C/L of fulvic or humic acid) ^c	
pH	pH = 5.5, 7.0, 8.5	

Note:

^a ionic strength, which is related to total dissolved solids (TDS), was achieved by adding NaNO₃

^b saturation index with respect to hydroxylpyromorphite (Pb₅(PO₄)₃OH), SI = Log (Q/Ksp), where Q is the actual dissolved composition, and Ksp is solubility product constant

Experimental



Characterization	Techniques
Morphology of precipitates	Scanning electron microscopy (SEM)
Phase identification of precipitates	Raman
Size and zeta potential measurements	Dynamic light scattering (DLS)

Dynamic light scattering (DLS)



Zetasizer (Malvern Instrument Ltd.) was used to measure the size evolutions and zeta potentials of lead phosphate particles.

Size measurements

Brownian motion of particles -> intensity of the light scattered fluctuates

↓ Analyze intensity fluctuation

Speed of Brownian motion

↓ Stokes-Einstein relationship

Particle size

Zeta potential measurements

Dispersion introduced into a cell containing two electrodes

↓ Apply an electrical field

Charged particles migrate towards oppositely-charged electrode -> measured electrophoretic mobility

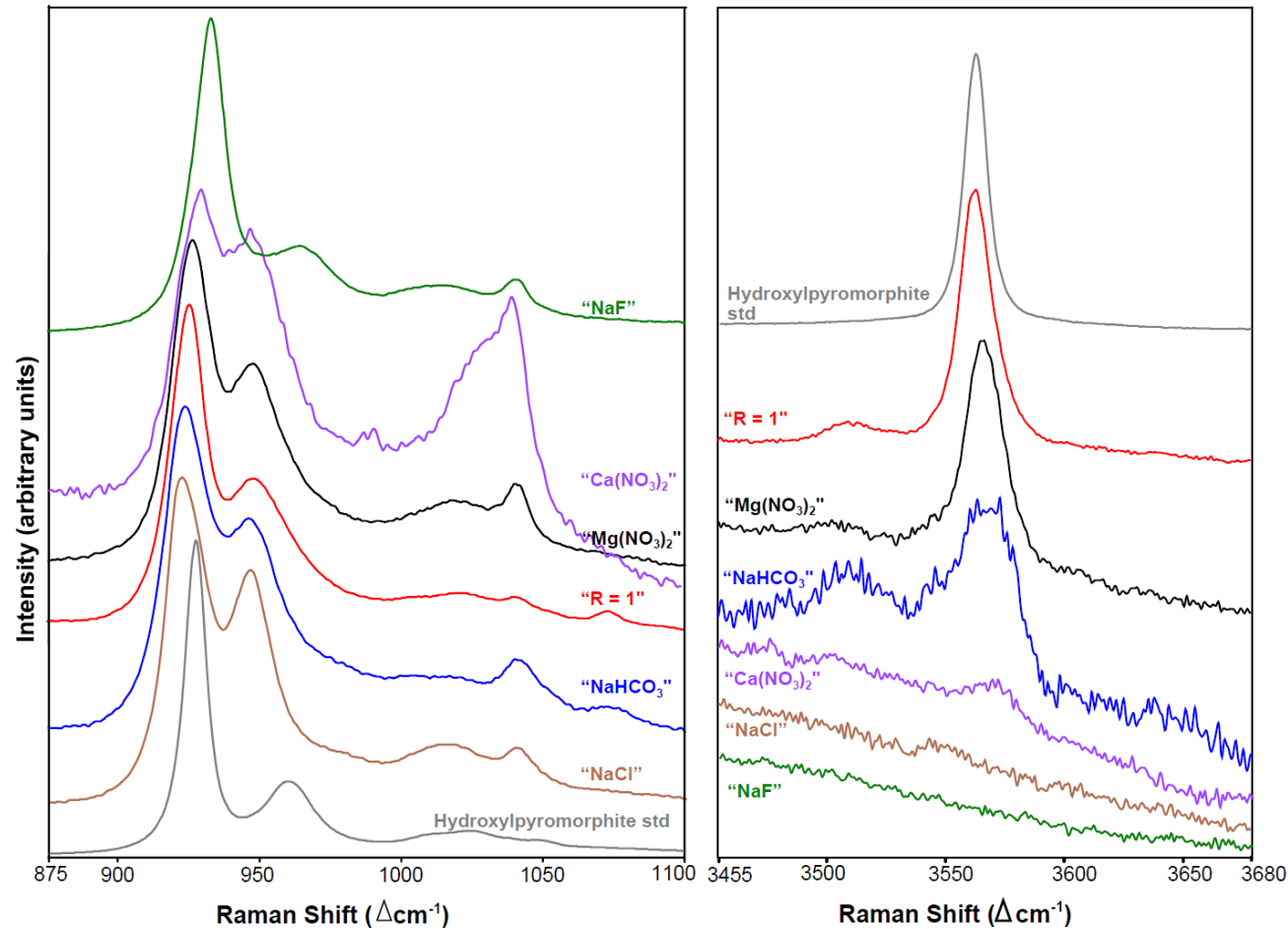
↓ Conversion

Zeta potential

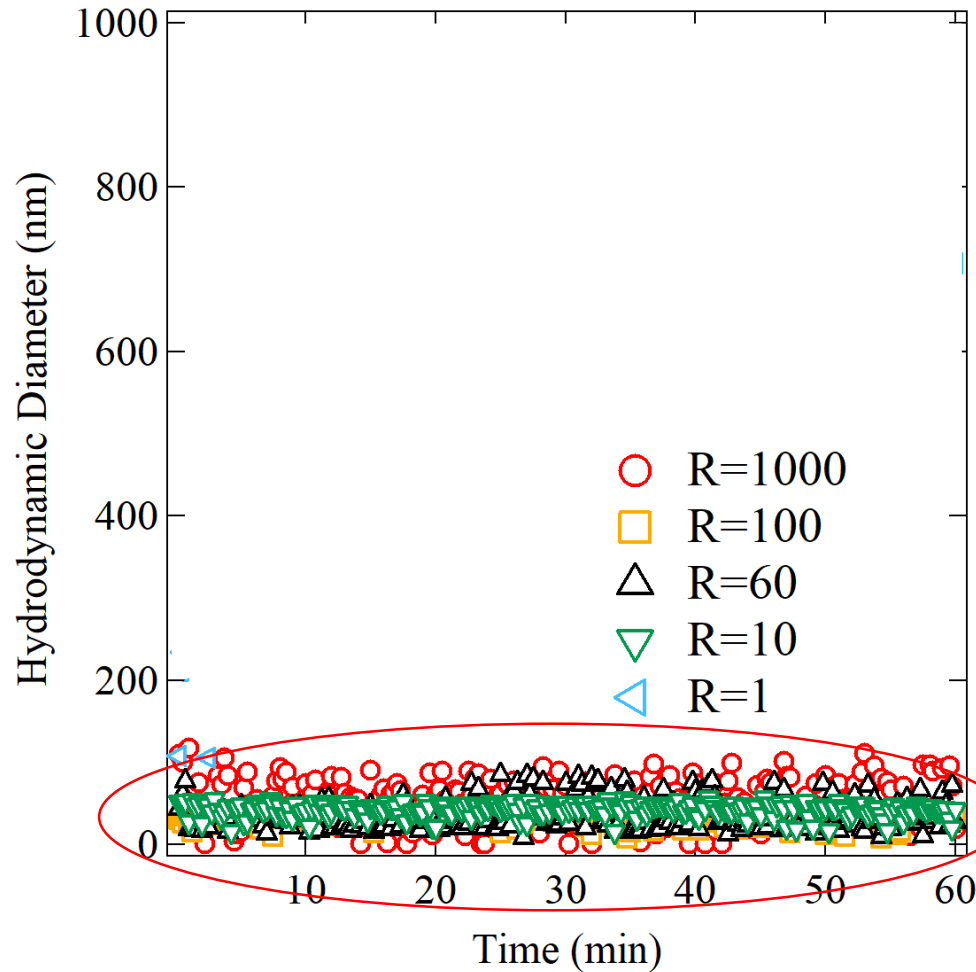
Phase identification of precipitates

Raman

1. Hydroxylpyromorphite formed in most solution conditions.
2. Chloropyromorphite and fluoropyromorphite formed in presence of Cl^- and F^- , respectively.



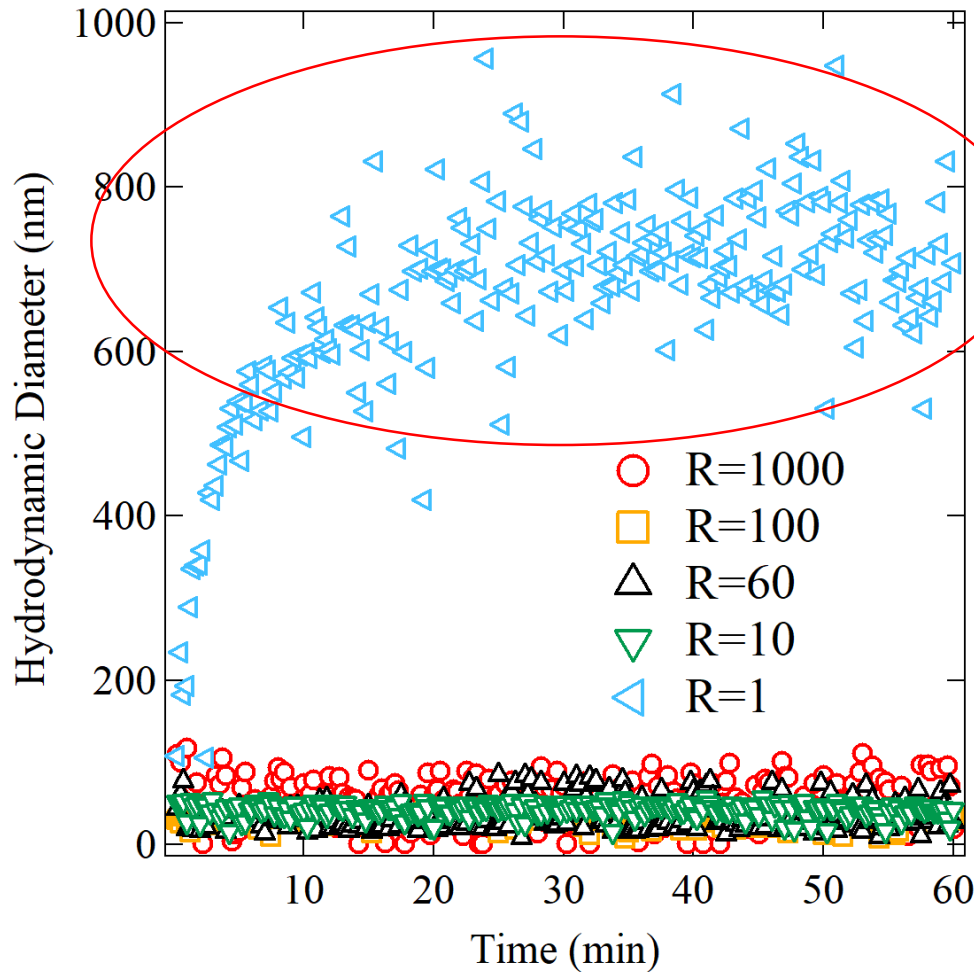
Effects of PO₄/Pb ratios



R _{P/Pb}	Zeta potential (ζ, mV)
1000	-37.8 ± 1.9
100	-32.0 ± 2.0
60	-33.1 ± 1.6
10	-31.0 ± 1.6

No significant aggregation for high R_{P/Pb} ratios (1000, 100, 60, and 10), as all particles were highly negatively charged.

Effects of PO₄/Pb ratios



$R_{P/Pb}$	Zeta potential (ζ , mV)
1000	-37.8 ± 1.9
100	-32.0 ± 2.0
60	-33.1 ± 1.6
10	-31.0 ± 1.6
1	-3.9 ± 2.1

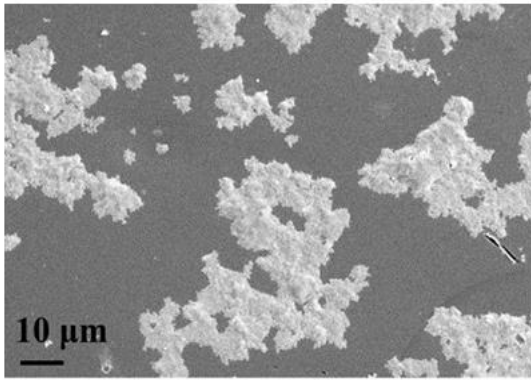
Fast aggregation occurred for low $R_{P/Pb}$ ratio (1), as particles were much less negatively charged.

Why did P/Pb ratio affect zeta?

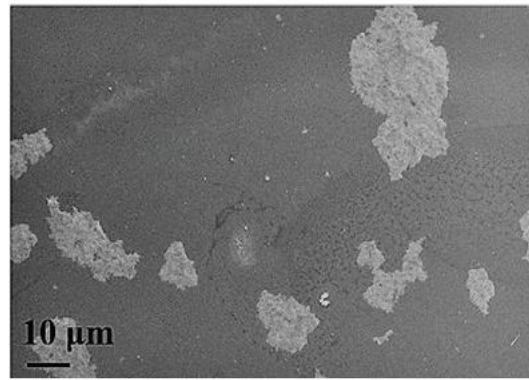


Morphology of precipitates

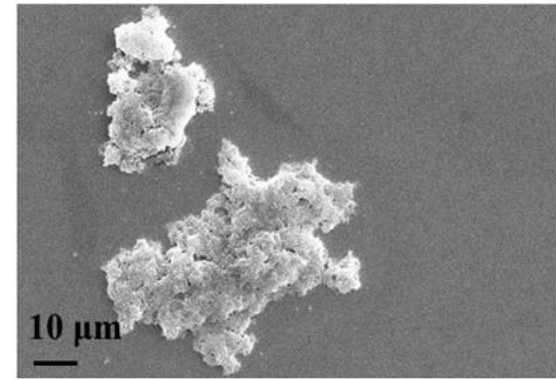
Scanning electron microscopy (SEM)



$$R_{P/Pb} = 1$$



In the presence of
1.2 mM $\text{Ca}(\text{NO}_3)_2$

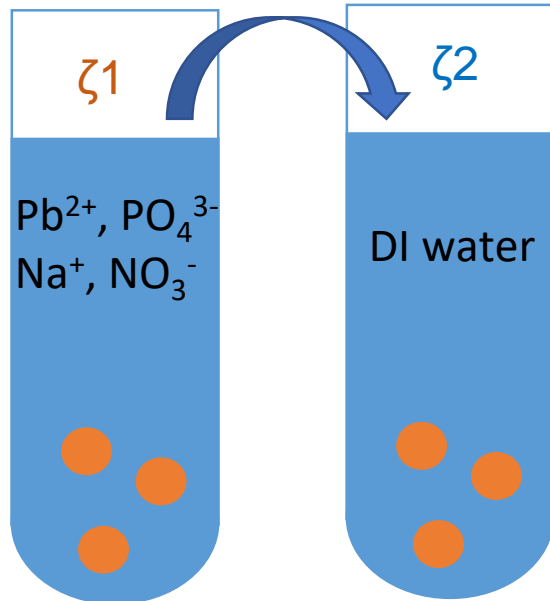


In the presence of
1.2 mM $\text{Mg}(\text{NO}_3)_2$

- These were aggregates of the particles, not individual particles.
- For $R_{P/Pb} > 1$, only small particles were observed. -> Aggregates observed by SEM were mainly formed in suspensions, rather than from drying-induced aggregation.

Effects of PO_4/Pb ratios

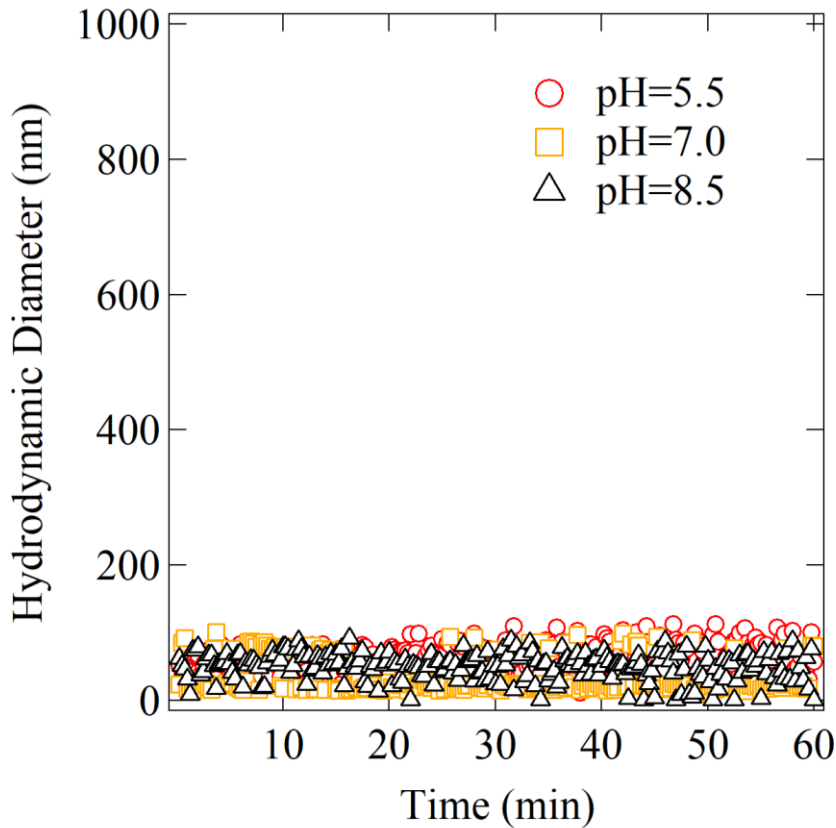
Centrifuge to collect precipitates,
rinse and then redisperse



$R_{\text{P/Pb}}$	ζ_1 (mV)	ζ_2 (mV)
1000	-37.8 ± 1.9	-15.6 ± 3.1
100	-32.0 ± 2.0	-17.5 ± 3.5
60	-33.1 ± 1.6	-15.0 ± 3.0
10	-31.0 ± 1.6	-9.0 ± 1.8
1	-3.9 ± 2.1	-8.5 ± 2.7

Under high $R_{\text{P/Pb}}$ ratios (1000 - 10), zeta potentials in precipitation solution (ζ_1) was more negative than in DI water (ζ_2), due to phosphate adsorption.

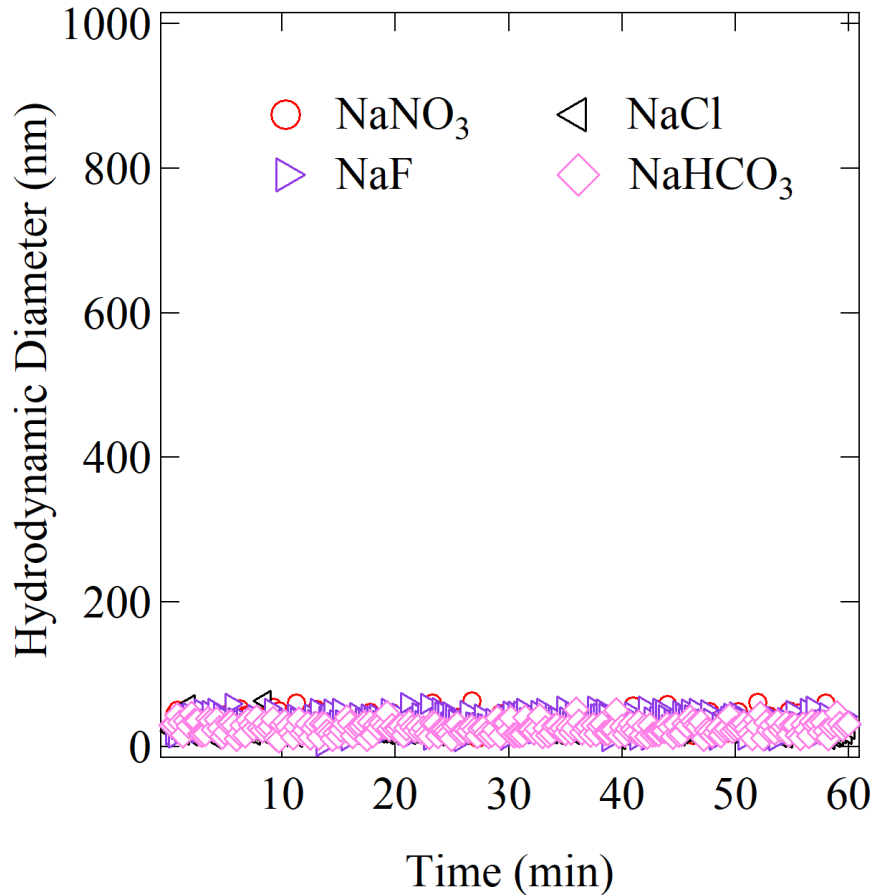
Effects of pH



pH	5.5	7.0	8.5
In precipitation solution	-31.7 ± 0.8	-32.0 ± 2.0	-23.6 ± 2.8

1. Particle sizes were similar under pH = 5.5, 7.0, and 8.5.
2. Zeta potentials in precipitation solution were similar, which could be due to the phosphate adsorption.

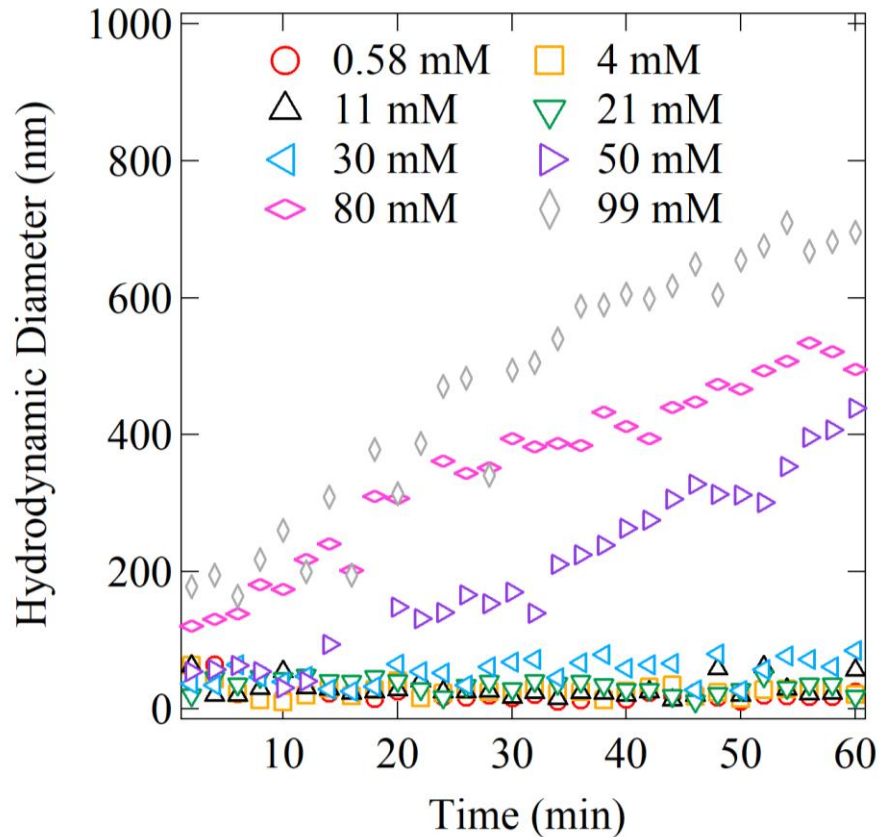
Effects of anions



1. No significant effects of anions on particle sizes were observed.
2. Chloropyromorphite and fluoropyromorphite had similar zeta potentials as hydroxylpyromorphite, resulting in similar aggregation behaviors.

ZP (mV)	3 mM NaNO ₃	3.2 mM NaF	3.6 mM NaCl	3.1 mM NaHCO ₃
ζ ₁	-32.0 ± 2.0	-26.4 ± 0.9	-25.1 ± 5.0	-26.6 ± 1.5

Effects of ionic strength (IS)



NaNO₃ was used to adjust ionic strength

IS (mM)	0.58	4	11
(mg/L)	49.3	340	935
IS (mM)	21	30	50
(mg/L)	1785	2550	4250
IS (mM)	80	99	
(mg/L)	6800	8415	

At all ionic strength values relevant to drinking water supply (< 10 mM), they would not be high enough with a 1:1 electrolyte to result in aggregation.

Effects of ionic strength (IS) - continued

Derjaguin–Landau–Verwey–Overbeek
(DLVO) theory

$$\downarrow V_{EDL} = 64\pi\epsilon_0\epsilon \frac{a_p}{2} \left(\frac{kT}{e}\right)^2 \left(\tanh \frac{e\psi_p}{4kT}\right)^2 \exp(-\kappa h) \downarrow$$

$$\uparrow \kappa = \sqrt{\frac{2N_A e^2 IS}{\epsilon_0 \epsilon_r k_B T}} \uparrow$$

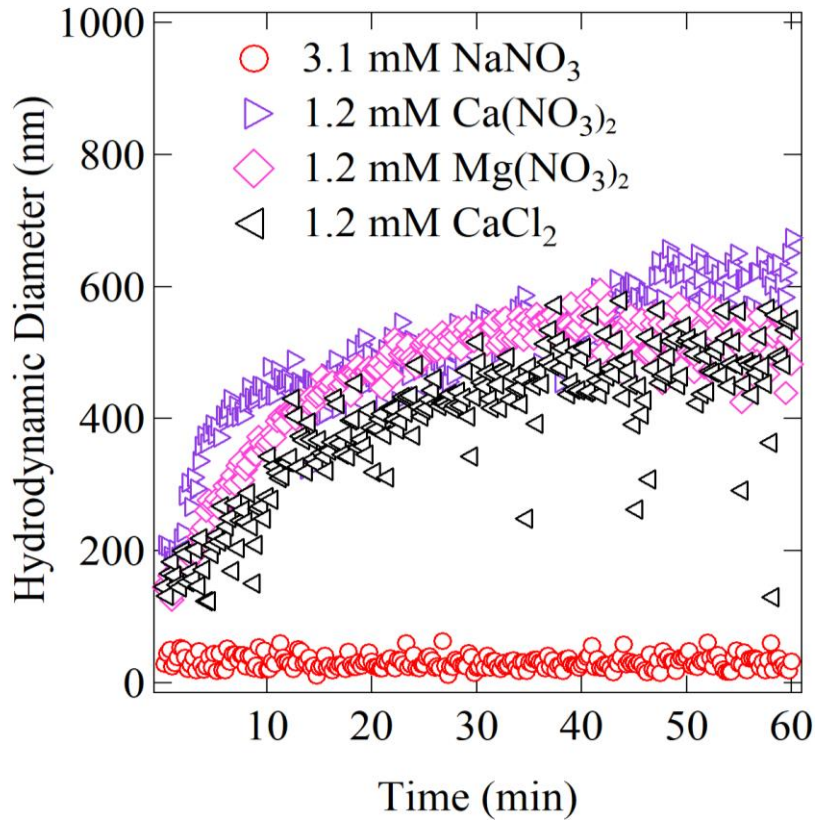
V_{EDL} : Electrical double layer repulsion

ψ_p : zeta potentials

κ^{-1} : Debye length

1. The zeta potentials did not change much (-34.1 ± 1.8 mV) under different IS: phosphate adsorption
2. Debye length decreased with the increase of IS, leading to smaller electrostatic repulsion and greater aggregation.

Effects of cations



	ζ (mV)
3 mM NaNO ₃	-32.0 ± 2.0
1.2 mM Ca(NO ₃) ₂	-10.3 ± 0.5
1.2 mM Mg(NO ₃) ₂	-10.9 ± 0.5
1.2 mM CaCl ₂	-11.0 ± 0.4

1. Compared with Na⁺, fast aggregation occurred in Ca²⁺ and Mg²⁺.

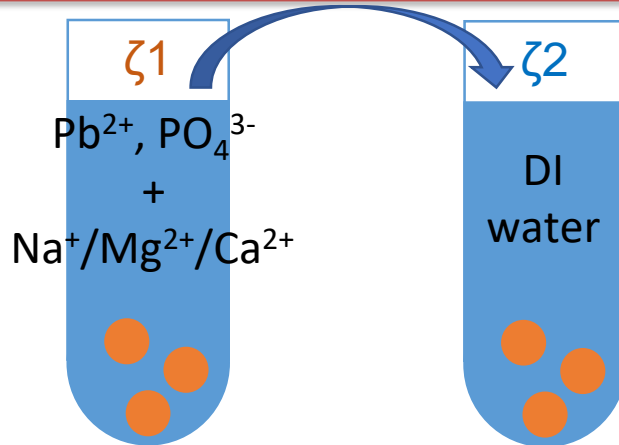
2. In Ca²⁺ and Mg²⁺, charges of particles were close to neutral. ?

(a) Structural incorporation

(b) Cation adsorption

Effects of cations

Centrifuge to collect precipitates from precipitation solutions, rinse and then redisperse them in DI water

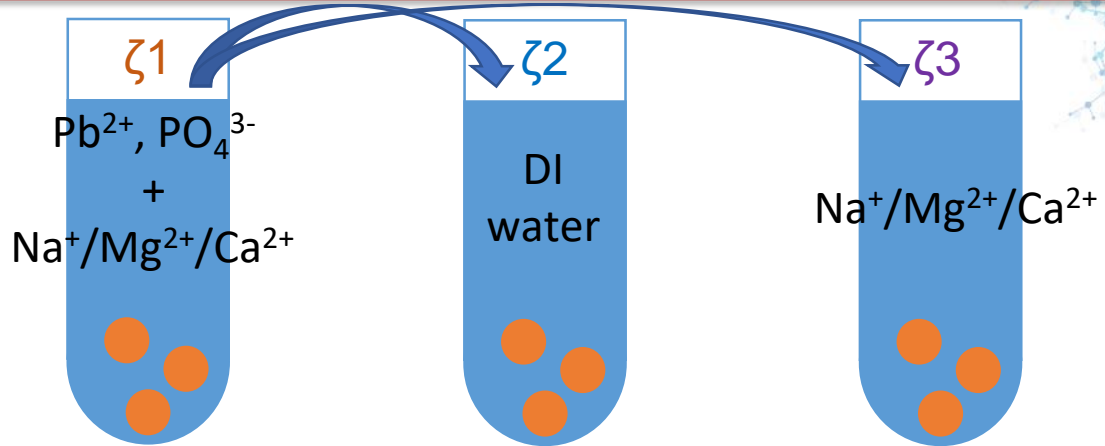


	$\zeta 1$ (mV)	$\zeta 2$ (mV)
3 mM NaNO_3	-32.0 ± 2.0	-17.5 ± 3.5
1.2 mM $\text{Ca}(\text{NO}_3)_2$	-10.3 ± 0.5	-20.2 ± 1.2
1.2 mM $\text{Mg}(\text{NO}_3)_2$	-10.9 ± 0.5	-19.5 ± 1.0
1.2 mM CaCl_2	-11.0 ± 0.4	-20.3 ± 1.0

Similar charges for particles in DI ($\zeta 2$): Structural incorporation, if occurred, was not controlling

Effects of cations - continued

Centrifuge to collect precipitates from precipitation solutions, rinse and then redisperse them in salt solutions

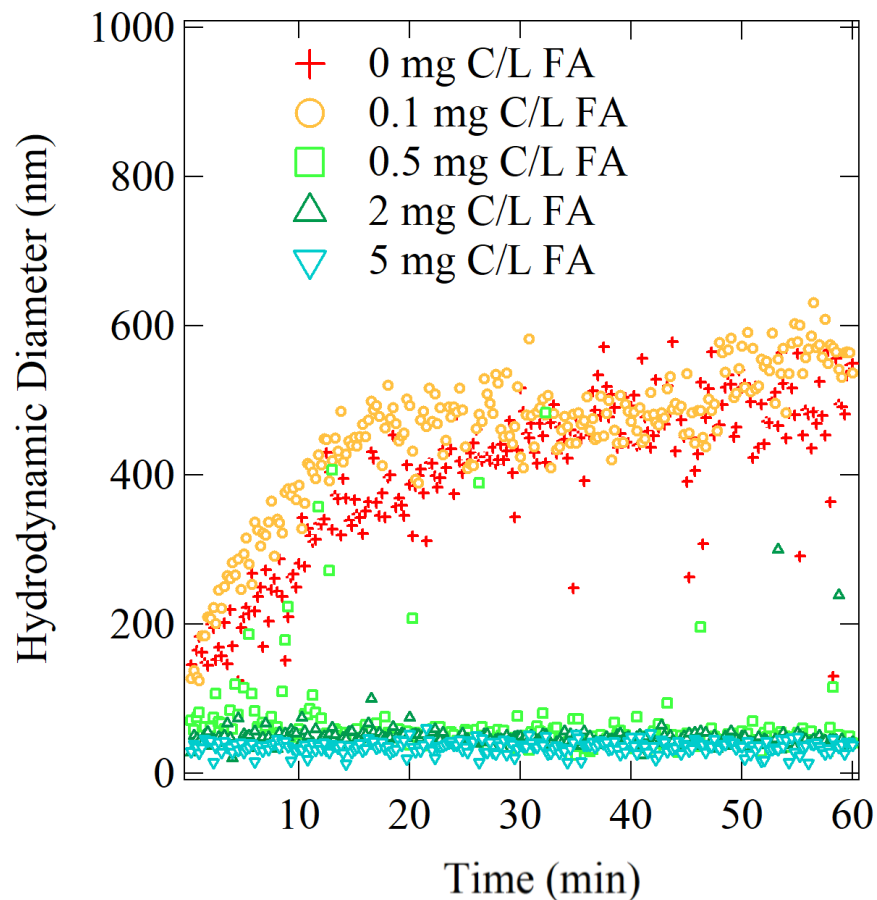


	$\zeta 1$ (mV)	$\zeta 2$ (mV)	$\zeta 3$ (mV)
3 mM $NaNO_3$	-32.0 ± 2.0	-17.5 ± 3.5	-9.9 ± 1.2
1.2 mM $Ca(NO_3)_2$	-10.3 ± 0.5	-20.2 ± 1.2	-4.7 ± 0.4
1.2 mM $Mg(NO_3)_2$	-10.9 ± 0.5	-19.5 ± 1.0	-4.7 ± 0.7
1.2 mM $CaCl_2$	-11.0 ± 0.4	-20.3 ± 1.0	-6.7 ± 1.2

Similarly less charged in salt solutions: Na^+ , Ca^{2+} & Mg^{2+} adsorption was similar
Phosphate adsorption promoted Ca^{2+} & Mg^{2+} adsorption.

Effects of NOM – fulvic acid

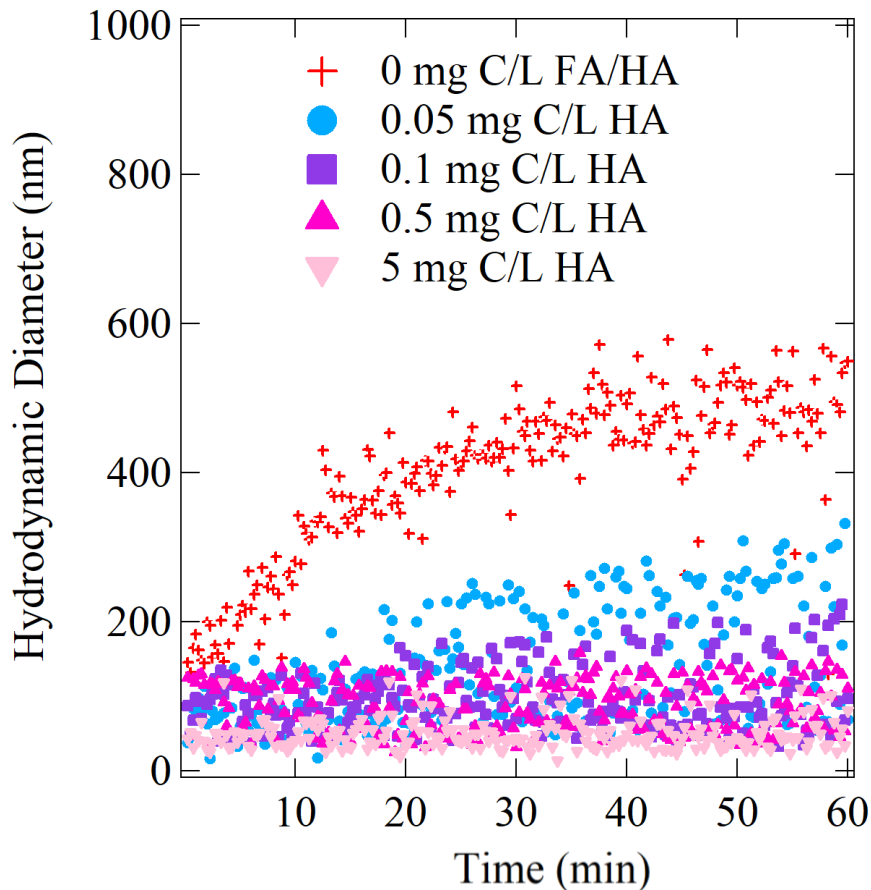
ZP (mV)	1.2 mM CaCl ₂	1.2 mM CaCl ₂ + (mg C/L) FA			
		0.1	0.5	2	5
In salt	-11.0 ± 0.4	-11.8 ± 1.4	-13.6 ± 0.6	-14.7 ± 0.4	-15.8 ± 0.8



Adding fulvic acid (FA, ≥ 0.5 mg C/L) inhibited aggregation.

Effects of NOM – humic acid

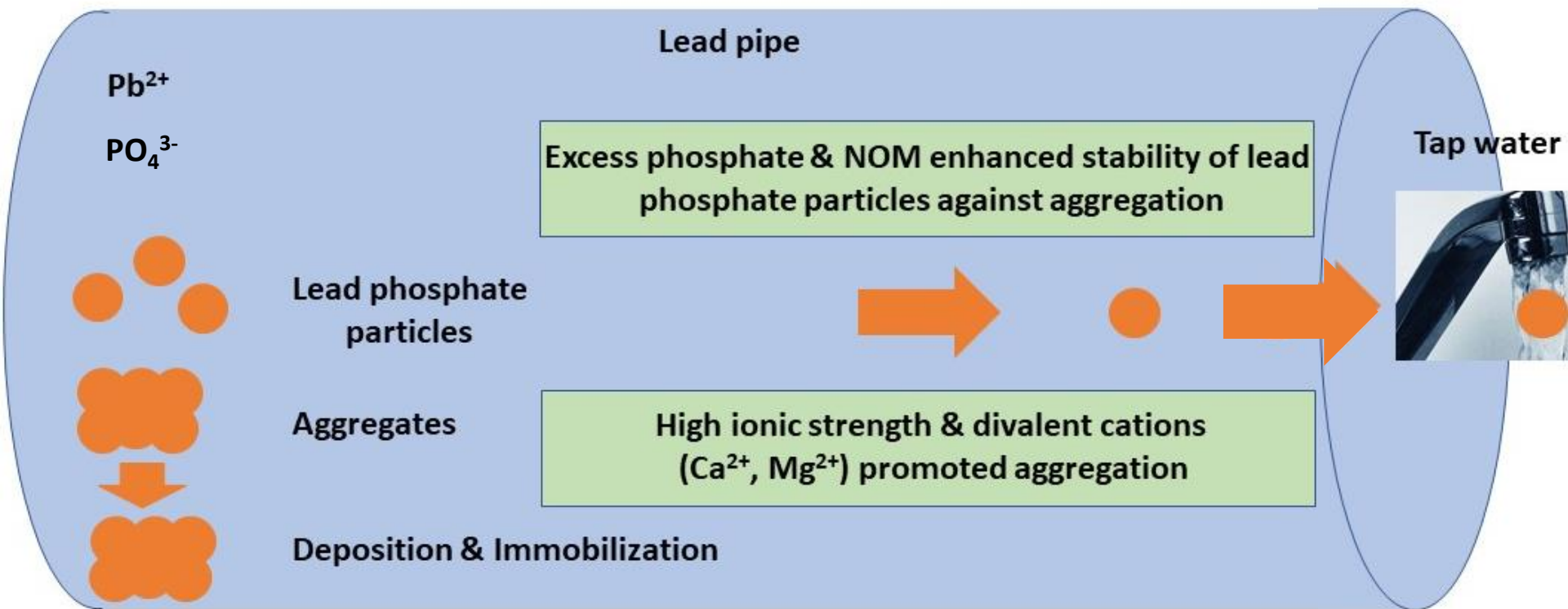
ZP (mV)	1.2 mM CaCl ₂	1.2 mM CaCl ₂ + (mg/L C) HA			
		0.05	0.1	0.5	5
In salt	-11.0 ± 0.4	-12.8 ± 1.1	-13.0 ± 0.7	-13.4 ± 0.5	-15.0 ± 0.3



Adding humic acid (HA, ≥ 0.05 mg C/L) inhibited aggregation.

- (a) NOM adsorb to particles, the deprotonated COO⁻ made surfaces more negatively charged, increasing electrostatic repulsion.
- (b) NOM coatings may cause steric repulsive forces between particles.

Conclusions



Environmental implications



- Unaggregated nanoparticles will be more mobile and may be less likely to be removed by a point-of-use filter.
- **Optimal phosphate dosage:** Excess amount of phosphate addition can lower dissolved lead concentration, however, it can also promote particulate lead transport along the pipes, and cause eutrophication.
- **Effects of Hardness:** Generation of stable lead phosphate particles that do not aggregate may be more likely in soft waters than in hard waters.
- **NOM removal:** Removal of NOM from drinking water can both limit formation of disinfection byproducts and promote lead phosphate aggregation.

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Thank you !!

Any Questions?



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