

Stability of Lead-Containing Precipitates: Implications for Lead Transport in Pipes and Soils

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DEDICATION/EPIGRAPH

In loving memory of my grandmother.

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ABSTRACT

Lead consumption can pose severe health risks to the public. To reduce lead exposure risks, phosphate addition is widely adopted to immobilize lead via the formation of lead phosphates with low solubility, especially pyromorphites such as hydroxylpyromorphite. However, the transport behavior of lead phosphate particles in response to their surrounding environment is not well understood. The overall objective of this dissertation research is to identify the key water chemistry parameters and mechanisms controlling the aggregation and deposition of lead phosphate particles in engineered and natural systems. The first study investigates lead phosphate formation and aggregation under conditions typical of drinking water supply systems. High aqueous PO_4/Pb molar ratios (> 1) enhanced the colloidal stability of the lead phosphate particles due to phosphate adsorption, whereas the presence of divalent cations (Ca^{2+} and Mg^{2+}) promoted the aggregation of lead phosphate particles at pH 7 via charge neutralization. However, such promoted aggregation was effectively countered by the presence of natural organic matter (NOM), which imparted steric repulsion. The second study investigates the deposition of lead phosphate particles under conditions representative of soil environments through column experiments. Clean bed filtration models failed to predict particle deposition since both ripening and straining occurred at ionic strengths ≥ 12.5 mM. The influences of the P/Pb ratio and the presence of Ca^{2+} and NOM on the aggregation and deposition behavior were consistent with that observed in the prior study. The third study investigates the influence of the molecular weight and chemistry of various types of NOM (two river NOM extracts, and soil and coal humic acid extracts) on the aggregation behavior of

lead phosphate particles. All types of NOM induced disaggregation and steric stabilization of the particles in the presence of Na^+ and low Ca^{2+} concentrations. However, for the soil and coal humic acid extracts, a threshold was observed where bridging flocculation (rather than steric stabilization) occurred at NOM concentrations ≥ 10 mg/L and Ca^{2+} concentrations ≥ 3 mM. Overall, this research demonstrates the importance of myriad mechanisms that must be considered to predict lead particle transport and exposure risks in applications of phosphate for lead remediation.

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CHAPTER 1. INTRODUCTION

1.1 Research Background and Current Limitations

Lead contamination has drawn great attention due to its ubiquity and the toxicity of lead. Remediation of lead contaminated sites remains a tough work, and phosphate is broadly applied as an effective approach to immobilize lead ascribing to the lead phosphate with low solubility formed. Transport of lead phosphate particles can determine the efficiency of phosphate addition. For instance, if lead phosphate particles keep stable in aqueous environments, they may travel a long distance along the pipe, leading to the long-lasting high lead levels in water supply systems. And if their mobility is high in soils, they may still be able to pass through the pores and ultimately pollute underground water. For this reason, it is crucial to study transport of lead phosphate particles subject to ambient environments. On the other hand, although the fate and transport behavior of engineered nanoparticles have been widely studied, information on lead phosphate particles formed in environmental remediation applications is limited.

Phosphate is commonly added to drinking water to inhibit lead release from lead service lines and lead-containing materials in premise plumbing. Phosphate addition promotes the formation of lead phosphate particles, and their aggregation behavior may affect their transport in pipes. Previous studies were mainly conducted in pilot-scale, finding that total lead concentrations remain high for months in pipes after adding phosphate, which consists with observations reported in several water crises. A research gap exists for influences of aqueous parameters on lead phosphate particles in water supply systems.

Similar to water supply systems, phosphate addition is commonly applied as an effective method to remediate lead contaminated sites due to formation of lead phosphate with low solubility. Various parameters have been reported to affect transport of particles, however, to our knowledge, there is a lack in studies focusing on their impacts on deposition behaviors of lead phosphate particles or on transport of particulate lead in porous media.

Apatite is commonly used to treat Pb-contaminated sites, and the main mechanism is dissolution of apatite and precipitation of pyromorphite. Organic matter, which is ubiquitous in waters and soils, is known to interfere with the aggregation of lead phosphate particles. To date, a few studies investigated the effect of low molecular weight organic acids (LMWOAs) on this process. However, systematic studies are needed on the effects of natural organic matter (NOM) extracts, which are more complex, on the aggregation process.

1.2 Hypotheses

1.2.1 Aggregation of Lead Phosphate Particles in Water Supply Systems

Based on prior studies on aggregation behaviors of other particles, we expect that high IS and divalent cations will promote aggregation of lead phosphate particles. It has been reported that NOM could adsorb onto various particles (e.g., iron oxide and zinc oxide) and inhibit their aggregation via both electrostatic and steric stabilization.¹⁻³ Therefore, we expect that NOM will retard aggregation of lead phosphate particles. Interactions among particles are described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, according to which the total energy barrier (V_T) for

particle aggregation is the sum of the electrostatic repulsive energy (V_{EDL}) and van der Waals (V_{VDW}) attractive energy. Whether the particles in suspension are stable or not is determined by the overall balance of attractive and repulsive energy. To understand the aggregation behaviors, electrostatic interactions among lead phosphate particles were considered. We expect that the zeta potentials of lead phosphate particles will be affected by aqueous parameters, thereby affecting their stability. If the phase of lead phosphate precipitates changes under certain conditions, we hypothesize it may also play a role on their aggregation behaviors. For example, in an *in situ* AFM study of the coupled cerussite dissolution and lead phosphate precipitation, Wang et al. found that the anions Cl^- and F^- substituted for the OH^- group in the lead phosphate precipitates, which affected the phase, size, and shape of the precipitates.⁴

1.2.2 Lead Phosphate Deposition in Porous Media

Based on prior studies on deposition behaviors of other particles, we expect that high IS and divalent cations will promote deposition of lead phosphate particles, whereas NOM will enhance transport of lead phosphate particles. Given findings discussed in Chapter 2, rapid aggregation occurred under low $R_{P/Pb}$. Thus, we expect that low $R_{P/Pb}$ will also facilitate deposition of lead phosphate particles. Since large aggregates formed at high IS may lead to straining during deposition process and DLVO does not account for ripening/straining processes, we hypothesize that clean-bed CFT can predict experimental results at low IS when accounting for DLVO interactions between only the particle and clean substrate. Contrarily, the predictions are expected

to fail at high ionic strength where particle-particle interactions (both in suspension and at the particle surface) can also become important.

1.2.3 Interactions Between Organics and Lead Phosphate Particles in Presence of Ca^{2+}

As Chapter 2 showed, the stability of lead phosphate particles increased with an increase in the concentration of humic/fulvic acids. Other researchers like Liu et al. also demonstrated similar effects of NOM concentration on aggregation of other nanoparticles.⁵ Taking these into account, we expect that the aggregation of lead phosphate particles in the presence of Ca^{2+} will also be dependent on NOM concentrations. Besides, Li et al. reported that high molecular weight (MW) NOM fractions stabilized ferrihydrite nanoparticles through steric repulsion ascribed to a higher mass adsorbed onto nanoparticles and larger size of high MW fraction.⁶ Hence, we expect aggregation of lead phosphate particles will also depend on NOM MW.

1.3 Dissertation Overview

This dissertation includes (1) investigating aggregation behaviors of lead phosphate particles in water supply systems, (2) measuring and predicting transport of particulate lead in soils when applying phosphate remediation strategies, and (3) studying the role of natural organic matter in controlling the aggregation of lead phosphate particles. The findings will contribute to a basic understanding of lead phosphate particle formation, provide useful information for optimization of lead immobilization strategies, and help predict transport of particulate lead.

In Chapter 2, the effects of aqueous P/Pb ratios, ionic strength, and pH, as well as the presence of cations (Na^+ , Ca^{2+} , and Mg^{2+}), anions (Cl^- , F^- , and HCO_3^-), and

natural organic matter (fulvic and humic acids) on lead phosphate aggregation are systematically investigated.

In Chapter 3, the effects of aqueous P/Pb ratios, ionic strength, as well as the presence of cations (Ca^{2+}), and natural organic matter (humic acid) on lead phosphate deposition are systematically investigated mainly through column experiments.

In Chapter 4, the combined influences of the NOM quality and concentration, along with the background electrolyte composition and concentration, on the aggregation behavior of lead phosphate particles, are explored.

Chapter 5 identifies future directions that arise from this research.

CHAPTER 2. FORMATION AND AGGREGATION OF LEAD PHOSPHATE PARTICLES: IMPLICATIONS FOR LEAD IMMOBILIZATION IN WATER SUPPLY SYSTEMS

2.1 Introduction

Lead consumption can pose severe health risk to the public by impairing human nervous, digestive, hematopoietic, cardiovascular, and urinary systems.^{7,8} Before 1986, lead pipes were used as service lines for water supply to connect buildings to water mains.⁹ Lead can be released into drinking water from lead pipes and scales of lead-containing corrosion products on the pipes, lead-bearing brass, copper/lead solder joints, and galvanized iron pipes.^{10–16} For lead corrosion control, an action level of 15 µg/L was set by the Lead and Copper Rule (LCR) for the total lead concentration in water systems serving more than 50,000 people.¹⁷

However, occurrences of elevated lead concentrations in tap water are common nation-wide mainly due to lead service lines (LSL) disturbance and water chemistry changes.^{18–20} A variety of water chemistry parameters can affect lead release from pipes, including pH, alkalinity, temperature, and the presence of iron particulates and NOM.^{21–30} Inadequate and inappropriate use of disinfectants and corrosion inhibitors can also lead to elevated lead concentrations in tap water.^{31–33} From 2001 to 2004, due to the switch of water disinfectants, high lead concentrations were observed in Washington DC tap water.^{33,34} During the recent water crisis in Flint, MI (started in April 2014), the lack of phosphate addition and switch of sulfate to chloride-based

coagulants resulted in extensive iron and lead release.³⁵ Lead concentrations over hazardous waste level of 5,000 µg/L were detected in tap water.³⁶

To control lead corrosion and release, water chemistry of the treated drinking water can be adjusted.^{37–43} Dissolved lead concentrations can be controlled by the dissolution/precipitation of lead corrosion products (e.g., lead oxides, carbonates, and phosphates). Among various corrosion inhibitors (e.g., phosphate, silicate, etc.), phosphate is the most widely used one to minimize lead corrosion in water supply systems.⁴⁴ In the absence of phosphates, cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) are common phases in pipe scale,⁴⁵ and dissolved lead concentrations in equilibrium with these phases can be higher than the action level (15 µg/L, 0.072 µM) of the Lead and Copper Rule. Phosphate addition can promote the precipitation of lead phosphate particles that are less soluble than lead carbonate phases and can provide equilibrium dissolved lead concentrations lower than 15 µg/L.^{41,46–48}

When phosphate has been added to control lead release, total lead concentrations (dissolved + particulate lead) in tap water were reported to remain high (over 50 µg/L) for months after phosphate addition.^{49–51} Pipe rig studies to evaluate the optimization of corrosion control treatment for the D.C. Water and Sewer Authority (DCWASA)'s distribution system indicated that it took six months of phosphate addition before lead concentrations consistently dropped below 15 µg/L.⁵⁰ Same observation was found in pipe systems of Providence, RI. After adding phosphoric acid for 5 months, high levels of total lead concentration occurred frequently, while dissolved lead concentrations decreased almost immediately and

stayed low.⁵¹ When the water crisis in Flint was reported, phosphate was added after its absence for 18 months. The total lead concentrations were reported to remain as high as 141 to 22,905 $\mu\text{g/L}$ at several residences for 6 months, which were 1-3 orders of magnitude higher than the action level (15 $\mu\text{g/L}$).⁵² These reported high concentrations of total lead in tap water after phosphate addition indicated the possible transport of lead phosphate particles along the pipes to taps.

Pilot-scale studies have been conducted to investigate lead immobilization after phosphate addition under conditions relevant to water supply systems.^{13,49,53} Churchill et al. conducted a 12-month pilot plant study and found that the total lead concentrations at the pipe outlet were higher than 15 $\mu\text{g/L}$ even after continuous phosphate addition for a half year.⁴⁹ Miller conducted pilot-scale experiments of orthophosphate addition with lead pipes, and it was reported that higher total lead removal efficiency was achieved with 1.0 mg PO_4/L instead of 5.0 mg PO_4/L addition.⁵³ Such observations showed that, although more phosphate addition can lower dissolved lead concentration, it might result in higher total lead concentration, suggesting the importance of transport of lead phosphate particles in pipes.

Effects of aqueous parameters (e.g., alkalinity and pH) on particulate lead stability in water supply systems have been studied without phosphate addition;^{21,54} However, the formation and aggregation of lead phosphate particles under varied aqueous conditions relevant to drinking water supply systems have not been studied yet. Based on Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and reported aggregation behaviors of other particles (e.g., magnetite, ferrihydrite and TiO_2), divalent cations generally promote particle aggregation by charge neutralization, while natural

organic matter has been reported to retard or promote aggregation depending on solution conditions.^{55–57} Ionic strength and pH also have great influence on aggregation behaviors of particles by affecting the thickness of the electric double layer and the surface protonation/deprotonation.^{55–57}

This study aims to provide new information on factors governing the aggregation of freshly precipitated lead phosphate particles using dynamic light scattering (DLS). To mimic processes in pipe systems where lead phosphate formation and aggregation occur simultaneously, here lead and phosphate solutions were mixed to study the formation of lead phosphate nanoparticles and their subsequent aggregation. The effects of aqueous P/Pb ratios, ionic strength, and pH, as well as the presence of cations (Na^+ , Ca^{2+} , and Mg^{2+}), anions (Cl^- , F^- , and HCO_3^-), and natural organic matter (fulvic and humic acids) on lead phosphate aggregation were systematically investigated. To understand the controlling mechanisms, the morphology, compositions, phase, and zeta potentials of the particles were measured using scanning electron microscopy (SEM), inductively coupled plasma mass spectrometry (ICP-MS), Raman spectroscopy/grazing-incidence wide-angle X-ray scattering (GIWAXS), and DLS, respectively. The new insights provided here can optimize phosphate addition to control lead release and mobilization from lead pipes.

2.2 Materials and Methods

2.2.1 Solution preparation

All solutions used in this study were prepared with ultrapure water (resistivity $> 18 \text{ m}\Omega$) equilibrated with atmospheric CO_2 (i.e., by purging with air overnight),

except for the NaHCO_3 solution which was prepared using ultrapure water without aeration. Stock solutions of 1 mM $\text{Pb}(\text{NO}_3)_2$, 10 mM Na_2HPO_4 , 10 mM NaH_2PO_4 , 100 mM NaNO_3 , 1.2 mM $\text{Ca}(\text{NO}_3)_2$, 1.2 mM $\text{Mg}(\text{NO}_3)_2$, 3.6 mM NaCl and 3.1 mM NaHCO_3 were prepared. Though the composition and properties of fresh-water NOM vary among different sites, the predominant species (from approximately 70 to > 90%) is reported to be humic substances (HS).⁵⁸ They are also considered as the most important components in relation to water treatment and corrosion processes.⁵⁹ Thus, fulvic acid and humic acid were used here as representatives of NOM, and their typical concentrations (0.1, 0.5, 2, and 5 mg C/L for fulvic acid and 0.05, 0.1, 0.5, 5 mg C/L for humic acid) in drinking water systems were chosen.^{60,61} Stock solutions of fulvic acid (Suwannee River) and humic acid (Sigma Aldrich) were prepared, and the organic carbon contents were determined with a total organic carbon (TOC) analyzer (TOC-L, Shimadzu). Details of NOM sample preparation and TOC measurements can be found in the Appendix A. The stock solutions were then diluted to the desired concentrations (**Table 2.1**) using CO_2 -equilibrated ultrapure water except for the NaHCO_3 solution.

Table 2.1. Initial experimental conditions and zeta potentials of precipitates

	Set	$R_{P/Pb}$	Pb ^a , μM	P ^a , mM	NO ₃ ⁻ , mM	Na ⁺ , mM	IS ^b , mM	pH ^b	Other saturated mineral phases ^c	ξ _p ^d , mV	ξ _w ^e , mV	ξ _s ^f , mV
I	R-1000	1000	1.40	1.40	1.66	3.78	4	7.0	N/A	-46.2 ± 2.3	-22.5 ± 4.5	N/A
	R-100	100	3.20	0.32	3.01	3.51	4	7.0	HCR	-39.1 ± 2.4	-25.2 ± 5.0	N/A
	R-60	60	3.70	0.222	3.56	3.94	4	7.0	Pb(OH) ₂ , HCR	-40.5 ± 2.0	-21.6 ± 4.3	N/A
	R-10	10	6.90	6.90×10^{-2}	3.76	3.92	4	7.0	Pb(OH) ₂ , CRU, HCR	-37.9 ± 2.0	-13.0 ± 2.6	N/A
	R-1	1	24.6	2.46×10^{-2}	3.85	3.87	4	6.7	Pb(OH) ₂ , CRU, HCR	-9.7 ± 2.7	-12.3 ± 2.5	N/A
II	1.2 mM Ca(NO ₃) ₂	100	3.20	0.32	2410	0.543	4	7.0	Pb(OH) ₂ , HCR, APT, HAP	-12.6 ± 0.6	-29.1 ± 1.7	-5.7 ± 0.5
	1.2 mM Mg(NO ₃) ₂	100	3.20	0.32	2410	0.552	4	7.0	Pb(OH) ₂ , HCR	-13.3 ± 0.6	-28.1 ± 1.4	-5.7 ± 0.9
	3.6 mM NaCl	100	3.40	0.34	6.80	4.14	4	7.0	HCR, CPM	-30.7 ± 6.1	-31.3 ± 2.6	-12.5 ± 1.7
	3.2 mM NaF	100	3.20	0.32	6.40	3.74	4	7.0	Pb(OH) ₂ , HCR, FPM	-32.3 ± 1.1	-26.0 ± 3.7	-11.1 ± 2.9
	3.1 mM NaHCO ₃	100	6.44	0.64	12.9	3.74	4	7.0	CRU, HCR	-32.5 ± 1.8	-29.4 ± 3.3	-18.7 ± 2.6
III	1.2 mM CaCl ₂	100	3.20	0.32	6.40	0.547	4	7.0	Pb(OH) ₂ , HCR, CPM, APT, HAP	-13.4 ± 0.5	N/A	N/A
	CaCl ₂ + FA	100	3.20	0.32	6.40	0.547	4	7.0	Pb(OH) ₂ , HCR, CPM, APT, HAP	-17.1 ± 2.1	N/A	N/A
	CaCl ₂ + HA	100	3.20	0.32	6.40	0.547	4	7.0	Pb(OH) ₂ , HCR, CPM, APT, HAP	-16.6 ± 1.2	N/A	N/A

(Table 2.1. continued)

IV	IS-0.58 – 99	100	3.00	0.30	6.00	0.471	0.58	7.0	Pb(OH) ₂ , HCR	-38.7 ± 2.6	N/A	N/A
			–	–	× 10 ⁻³	–	–					
			9.10	0.91	– 100	101	99					
V	pH-5.5	100	36	3.60	7.20 × 10 ⁻²	3.71	4	5.5	N/A	-38.7 ± 1.0	-13.6 ± 1.4	N/A
	pH-8.5	100	4.40	0.44	1.01	3.55	4	8.5	Pb(OH) ₂ , CRU, HCR	-27.3 ± 3.4	-14.1 ± 1.4	N/A

Note: Pb^a and P^a: calculated total lead and phosphate concentrations, which were consistent with measurements using ICP-MS. IS^b (Ionic Strength) and pH^b were calculated using GWB based on initial solution conditions. Conductivity and pH were measured at the beginning and end of the DLS measurements, and no significant differences were observed. Other saturated mineral phases^c: All solutions were supersaturated with three pure lead phosphate phases (hydroxylpyromorphite, Pb₃(PO₄)₂, and PbHPO₄). Here, other saturated mineral phases are listed, where HCR, CRU, APT, HAP, CPM, and FPM represent hydrocerussite, cerussite, apatite, hydroxyapatite, chloropyromorphite, and fluoropyromorphite, respectively. Detailed information of the calculated saturation indices (SI) for all minerals can be found in the Appendix A. ξ_p^d : zeta potentials of particles in precipitation solutions. ξ_w^e : zeta potentials of particles in water. ξ_s^f : zeta potentials of particles in salt solutions as illustrated in **Figure A.3**.

Here, five sets of experiments were conducted (**Table 2.1**) to investigate the effects of total P/Pb ratios ($R_{P/Pb} = 1000, 100, 60, 10$, and 1 , set I), cations and anions (Na^+ , Ca^{2+} , Mg^{2+} , NO_3^- , Cl^- , F^- , and HCO_3^- , set II), natural organic matter (fulvic acid with $0.1, 0.5, 2$, and 5 mg C/L, and humic acid with $0.05, 0.1, 0.5$, and 5 mg C/L, set III), ionic strength ($IS = 0.58, 4, 11, 21, 30, 50, 80$ and 99 mM, set IV), and pH ($5.5, 7.0$, and 8.5 , set V) on lead phosphate formation and aggregation in solutions equilibrated with atmospheric CO_2 except for the experiment with $NaHCO_3$ solution. The mixtures of Na_2HPO_4 and NaH_2PO_4 solutions were used as the phosphate source and to adjust solutions' pH, and $NaNO_3$ was used to adjust solutions' ionic strength. Although ionic strength values greater than 11 mM are unlikely in drinking water, they were included in set IV to study the overall effects of ionic strength on the particle aggregation. For solutions with the addition of salts (sets II and IV) and NOM (set III), the Na_2HPO_4/NaH_2PO_4 solutions were first mixed with salt solution ($NaNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $CaCl_2$, $NaCl$, NaF , or $NaHCO_3$) or organic matter (fulvic or humic acid) and the mixed solution was vortexed for 5 s. Then $Pb(NO_3)_2$ solution was added to the mixed solution and lead phosphate precipitation started in the presence of salts or organics. To prepare a solution at pH 8.5 for experiment set V, Na_2HPO_4 was first mixed with $NaOH$, and then $Pb(NO_3)_2$ solution was added to the mixed solution. The effects of various concentrations (i.e., $0.1, 0.5$, and 0.8 mM) of Ca^{2+} and Mg^{2+} on lead phosphate aggregation were also conducted, with detailed solution conditions in the Appendix A (**Table A.3**).

The solutions' pH, IS, and saturation index (SI) with respect to potential precipitates, i.e., $Pb_3(PO_4)_2$, $PbHPO_4$, pyromorphite-group minerals ($Pb_5(PO_4)_3OH$,

$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, and $\text{Pb}_5(\text{PO}_4)_3\text{F}$), cerussite, hydrocerussite, and lead hydroxide ($\text{Pb}(\text{OH})_2$) were calculated using the Minteq database in Geochemist's Workbench (GWB, student version 11.0) (**Table 2.1**), with all solutions set to be in equilibrium with atmospheric CO_2 except for the NaHCO_3 solution. In pipes from real drinking water distribution systems after phosphate treatment, as well as in new pipes used in experiments after phosphate addition, Pb-orthophosphate minerals, such as chloropyromorphite and hydroxylpyromorphite, have been identified as corrosion scales.⁶²⁻⁶⁴ In real drinking water systems, the initial total lead concentrations before treatment can be over the range of 50-5,000 $\mu\text{g/L}$,^{36,62,63} and a great excess of phosphate (0.6-8.6 mg/L) relative to lead is added.^{62,63} Here the initial SI with respect to hydroxylpyromorphite was estimated for a drinking water system equilibrated with air and having a solution pH of 7 and dissolved lead concentration of 100 $\mu\text{g/L}$, which is quite possible for a system that is out of compliance with the lead and copper rule (LCR). When a realistic dose of 3 mg/L phosphate is added for lead control, the initial SI with respect to hydroxylpyromorphite is calculated to be 10.7. To generate enough particles for accurate DLS measurements, here relatively higher lead and phosphate concentrations (**Table 2.1**) were used and the initial solutions' SI with respect to hydroxylpyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$) were similar (12.6 ± 0.1) in all solutions (**Table 2.1**). To separately investigate the effects of each water chemistry parameter ($R_{\text{P/Pb}}$, IS, cation/anion, NOM, or pH) for each set of experiments, solutions were prepared with fixed values for most of the other water chemistry parameters (**Table 2.1**).

2.2.2 Dynamic Light Scattering (DLS) Measurements

The formation and aggregation behaviors of particles formed in solution (**Table 2.1**, sets I-V) were explored by monitoring their size evolution in solutions by DLS (Zetasizer, Malvern Instrument Ltd.). Freshly prepared solution (**Table 2.1**) was shaken by hand for 5 s and then injected into a 1-mL cuvette (ZEN0040, Malvern Instruments Ltd.). Size data were continuously collected every 15 s for 1 h. In solutions with slow aggregation kinetics (i.e., no significant size changes within 1 h), sizes of particles were also measured daily for 12 days to understand the long-term aggregation. The sizes of lead phosphate particles were reported by number-based calculation using the refractive index of lead phosphate (2.048). To observe the morphology of particles in suspension, particles were collected from the precipitation/aggregation solutions (**Table 2.1**) by centrifuging at 5000 rpm for 1 minute, and the slurry was transferred to gold-coated silicon wafers. The wafers were then dried in a desiccator, and coated with gold before scanning electron microscopy (SEM, JEOL Ltd.) measurements. The detailed information about SEM measurements can be found in the previous publication and the Appendix A.⁶⁵

After the size measurement, the cuvette was equipped with a dip cell (ZEN1002, Malvern Instruments Ltd.) for electrophoretic mobility measurement of particles in all precipitation solutions (ξ_p , **Table 2.1**).^{66–72} Zeta potential values (ξ) were calculated based on the following relationship with the measured electrophoretic mobility (U_E) as

$$U_E = \frac{2\varepsilon\xi f(\kappa a)}{3\eta}, \quad (2.1)$$

where U_E = electrophoretic mobility ($V \cdot s \cdot m^{-2}$), ξ = zeta potential (V), ϵ = dielectric constant, η = viscosity ($m^2 \cdot s^{-1}$) and $f(\kappa a)$ = Henry's function with κ being Debye constant (nm^{-1}) and a being the size of the particles (nm).⁷³ Triplicate experiments were conducted, and the average and standard deviation values are shown in **Table 2.1**.

In addition, for set I, the effects of total P/Pb ratios on the zeta potentials of the precipitates could be due to the potential adsorption of lead or phosphate ions onto the precipitates. To understand such processes, the particles were collected from 50 mL precipitation solutions (**Table 2.1**, set I) using centrifugal filters (Amicon-15, Millipore), and were rinsed with ultrapure water multiple times to remove the adsorbed ions. Then the slurry was transferred to ultrapure water (pH $\sim$ 7, adjusted using NaOH) using a pipette, and zeta potential values (ξ_w , **Table 2.1**) were measured after sonicating for 30 min. Similarly, for set V, particles were collected from 50 mL precipitation solutions (**Table 2.1**, set V) and rinsed with ultrapure water. Then, the particles were dispersed in water with pH adjusted to that of the precipitation solution conditions (i.e., pH = 5.5, 7.0, and 8.5), and the zeta potential values (ξ_w , **Table 2.1**) were measured. There is a caveat that the particles collected after centrifuging and rinsing with water might have altered water chemistry in the near-surface region. However, the phosphate concentration in the near surface region should be still much lower than that in the original suspensions which had a great excess of phosphate.

For set II, to understand the effects of different electrolyte solutions on zeta potentials of the precipitates, particles were collected from 50 mL precipitation solutions (**Table 2.1**, set II) using centrifugal filters (Amicon-15, Millipore) and rinsed with ultrapure water multiple times. Then the collected particles were dispersed both

in ultrapure water (ξ_w , **Table 2.1**) and the salt solutions (ξ_s , **Table 2.1**, in 3 mM NaNO₃, 1.2 mM Ca(NO₃)₂, 1.2 mM Mg(NO₃)₂ with IS = 4 mM and pH = 7) for zeta potential measurements. A schematic illustration of the three different types of zeta potential measurements of the precipitates conducted in precipitation solutions, ultrapure water (equilibrated with air and with pH adjustment), and salt solutions (ξ_p , ξ_w , and ξ_s , **Table 2.1**) is provided as **Figure A.2** in the Appendix A.

2.2.3 Phase and Composition Analysis of Particles Formed in Solutions

Based on GWB calculations, the three pure lead phosphate phases (i.e., hydroxylpyromorphite, Pb₃(PO₄)₂, and PbHPO₄) were supersaturated under all initial solution conditions (**Table 2.1**), while some initial solutions (**Table 2.1**) were also saturated with other phases, which are listed in **Table 2.1**. Detailed information of the saturation indices with respect to all supersaturated mineral phases can be found in the Appendix A (**Tables A.1, A.2**). To identify the mineral phases of the precipitates, particles were collected from the precipitation solutions using centrifugal filters (Amicon-15, Millipore) and were transferred to a gold-coated silicon wafer for GIWAXS (beamline 12 ID-B at Advanced Photon Source (APS), Argonne National Laboratory) and Raman spectroscopy measurements. Detailed information on the GIWAXS and Raman spectroscopy measurements is available in the Appendix A. In the presence of Ca²⁺ and Mg²⁺, to study the potential structural incorporation and surface enrichment of these ions in the precipitates, chemical composition analysis of the precipitates was conducted with ICP-MS (details in the Appendix A).

2.3 Results and Discussion

2.3.1 Excess PO₄ Addition Stabilized Lead Phosphate Particles

Based on GWB calculations (**Table A.1**), all initial solutions in set I (**Table 2.1**) were supersaturated with respect to hydroxylpyromorphite ($SI = 12.6 \pm 0.1$), $Pb_3(PO_4)_2$ ($SI = 7.4 \pm 0.2$), and $PbHPO_4$ ($SI = 1.6 \pm 0.3$). In addition, the initial solutions with $R_{P/Pb} = 10$ and 1 (R-10 and R-1 in **Table 2.1**) were supersaturated with respect to cerussite ($SI = 0.3$) and hydrocerussite ($SI = 1.6$), and the initial solutions with $R_{P/Pb} = 60$, 10 and 1 (**Table 2.1**) were supersaturated with respect to lead hydroxide, cerussite and hydrocerussite. However, GIWAXS and Raman measurements (**Figure 2.1**) showed that hydroxylpyromorphite, with the highest SI, was the only mineral phase detected under all solution conditions of set I. Under the initial solution conditions, hydroxylpyromorphite which had the highest SI could precipitate out first. After the precipitation of hydroxylpyromorphite, lead ions were consumed and the SI values with respect to other mineral phases should decrease such that the final solution could be no longer supersaturated with respect to other lead-containing minerals. Therefore, although most of the initial solutions were supersaturated with respect to multiple mineral phases, hydroxylpyromorphite was the only mineral phase detected.

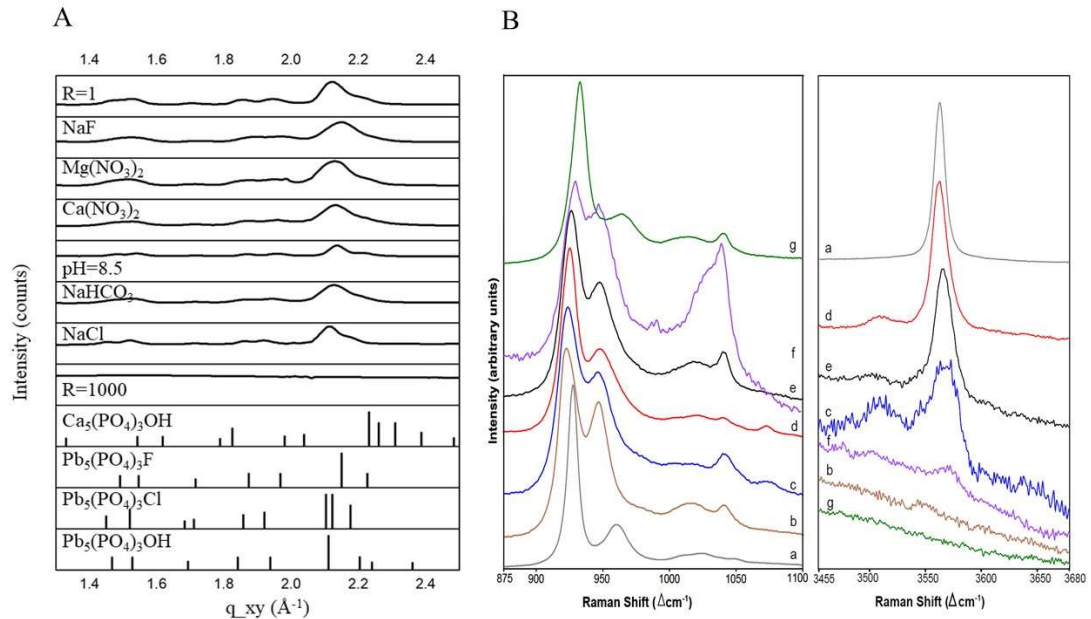


Figure 2.1. Phase identification of precipitates (A) GIWAXS measurements and (B) Raman spectroscopy.

The size evolution of particles formed in solutions with varied total PO_4/Pb molar ratios ($R_{\text{P/Pb}}$, set I in **Table 2.1**) are shown in **Figure 2.2A**. With $R_{\text{P/Pb}} \geq 10$ (i.e., $R_{\text{P/Pb}} = 1000, 100, 60$, and 10), the sizes of particles (40 ± 18 nm) remained unchanged within 1 h. Size measurements were also conducted for a longer time, and no significant size increase was observed up to 12 days (**Figure A.1**). In contrast to results with excess phosphate relative to lead, in a solution with $R_{\text{P/Pb}} = 1$, the sizes of the particles grew rapidly to 806 ± 39 nm in 1 h (**Figure 2.2A**). The initial fast size increase is indicated by the red line in **Figure 2.2A**. Later on, the size reaches plateau (**Figure 2.2A**), probably due to that DLS can only accurately measure particles < 1 μm .⁷⁴ Here large particles (> 10 μm , **Figure 2.3**) formed in solution with $R_{\text{P/Pb}} = 1$ as observed by SEM. SEM observations showed that the big particles were large aggregates of small crystals and not big crystals themselves. Therefore, the fast increase

in size of particles formed under $R_{P/Pb} = 1$ (**Figure 2.3A**) was due to fast particle aggregation rather than growth. While for the particles collected from solutions with $R_{P/Pb} > 1$ using the same centrifuging and drying procedures, only small particles and no aggregates were observed by SEM. Therefore, that the aggregates observed by SEM were formed in suspensions, not an artifact of centrifuging or drying the samples in preparation for SEM imaging.

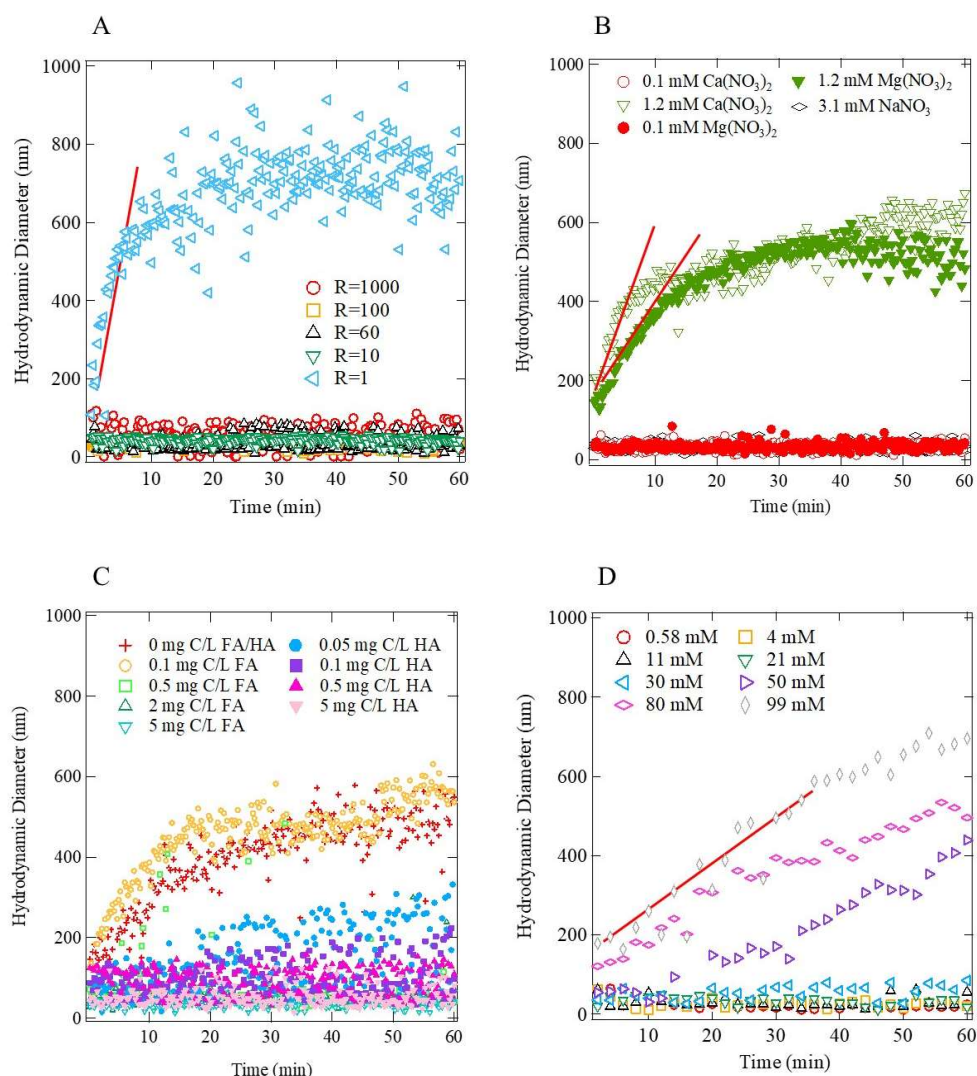


Figure 2.2. DLS measurements of size evolutions of lead phosphate particles within 1 h. (A) $R_{P/Pb}$ 1000 - 1, (B) in 1.2 mM $\text{Ca}(\text{NO}_3)_2$, 1.2 mM $\text{Mg}(\text{NO}_3)_2$, or 1.2 mM CaCl_2 , (C) in 1.2 mM CaCl_2 with 0-5 mg C/L fulvic or humic acid, (D) IS 0.58 - 99 mM.

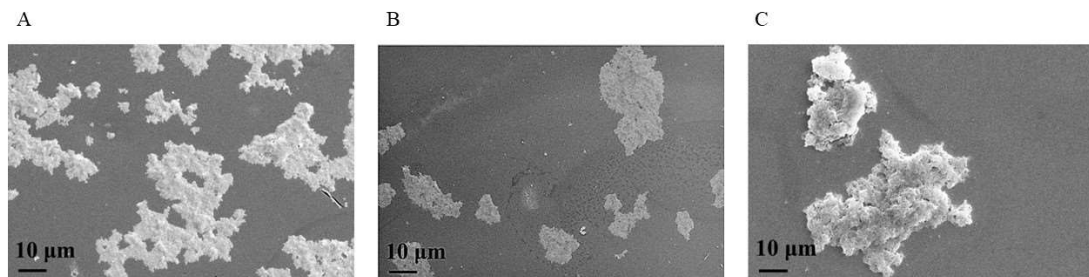


Figure 2.3. SEM observations of aggregates formed under varied solution conditions: (A) $R_{P/Pb} = 1$, (B) in the presence of 1.2 mM $\text{Ca}(\text{NO}_3)_2$, and (C) in the presence of 1.2 mM $\text{Mg}(\text{NO}_3)_2$.

Interactions among particles are described by DLVO theory, according to which the total energy barrier (V_T) for particle aggregation is the sum of the electrostatic repulsive energy (V_{EDL}) and van der Waals (V_{VDW}) attractive energy. Whether the particles in suspension are stable or not is determined by the overall balance of attractive and repulsive energy. To understand the aggregation behaviors, electrostatic interactions among lead phosphate particles were considered. Since Hamaker constant for hydroxylpyromorphite was not reported before, V_T for particle aggregation could not be calculated. In general, particles with absolute values of the zeta potential lower than 20 mV show relatively fast aggregation, and particles with absolute values of the zeta potential higher than 20 – 30 mV show good colloidal stability.^{75–77} Zeta potential measurements showed that in precipitation solutions with $R_{P/Pb} = 1000$, 100, 60, and 10, the particles were highly negatively charged with zeta potential values of -46.2 ± 2.3 , -39.1 ± 2.4 , -40.5 ± 2.0 , and -37.9 ± 2.0 mV, respectively (ξ_p , **Table 2.1**). Thus, the strong electrostatic repulsive forces among the particles prevented their aggregation in solution. In contrast, for $R_{P/Pb} = 1$, the particles were only slightly

negatively charged (-9.7 ± 2.7 mV), leading to very weak repulsive forces among the particles and thus their fast aggregation.

As hydroxylpyromorphite formed in all precipitation solutions (**Figure 2.1**), the varied zeta potentials of the precipitates measured in precipitation solutions (ξ_p) with varied $R_{P/Pb}$ were thought to be affected by the adsorption of lead and phosphate ions onto the precipitates. To test this hypothesis, the precipitates were collected from solution, rinsed with ultrapure water multiple times to remove the adsorbed lead and phosphate ions, and dispersed in water (equilibrated with air, pH adjusted to 7.0 by adding NaOH) for zeta potential measurements (ξ_w). For solutions with excess phosphate relative to lead, i.e., $R_{P/Pb} = 1000, 100, 60$, and 10 (set I in **Table 2.1**), the zeta potentials of precipitates measured in water after the rinsing steps (pH = 7.0) were -22.5 ± 4.5 , -25.2 ± 5.0 , -21.6 ± 4.3 , and -13.0 ± 2.6 mV (ξ_w , **Table 2.1**), which were much less negative than the zeta potentials measured in the precipitation solutions with lead and phosphate ions (ξ_p , **Table 2.1**, -46.2 ± 2.3 , -39.1 ± 2.4 , -40.5 ± 2.0 , and -37.9 ± 2.0 mV). In contrast, for the precipitates collected from solutions with $R_{P/Pb} = 1$, their zeta potential values in water after rinsing were -12.3 ± 2.5 mV (ξ_w , **Table 2.1**), similar to their zeta potential (ξ_p , **Table 2.1**, -9.7 ± 2.7 mV) measured in the precipitation solution with equal amounts of total lead and phosphate ions. Therefore, it can be concluded that in precipitation solutions with high aqueous P/Pb ratios, the adsorption of excess amounts of phosphate ions onto the precipitates made the lead phosphate particles highly negatively charged (ξ_p , **Table 2.1**), resulting in their enhanced aqueous stability. In a pilot-scale study with new lead pipe-loops treated with orthophosphate ranging from 0.5 to 5.0 mg PO₄/L, Miller found the lowest total

lead concentration with 1.0 mg PO₄/L addition and not with the highest phosphate addition (5.0 mg PO₄/L), suggesting higher total lead concentration in water with excess phosphate addition.⁵³ Our observation here suggested that the stability of lead phosphate particles was enhanced with excess phosphate addition, which might help explain Miller's pilot-scale observations in pipes. However, more future studies with pipe loops are needed to fully understand the effects of phosphate dosage on particulate lead immobilization.

2.3.2 Promoted Lead Phosphate Aggregation in the Presence of Ca²⁺ and Mg²⁺

Based on GWB calculations (**Table A.2** in Appendix A), both initial solutions in the presence of Ca(NO₃)₂ and Mg(NO₃)₂ were supersaturated with respect to hydroxylpyromorphite (SI = 12.6), Pb₃(PO₄)₂ (SI = 7.4), PbHPO₄ (SI = 1.6), lead hydroxide (SI = 0.1), and hydrocerussite (SI = 0.2). Besides, the initial solution in the presence of Ca(NO₃)₂ was also supersaturated with hydroxyapatite (Ca₃(PO₄)₅OH, SI = 7.7) and Ca₃(PO₄)₂ (SI = 0.9) (**Table 2.1**, set II). Meanwhile, researchers have reported that significant amounts of Ca ions can be incorporated in the hydroxylpyromorphite structure forming a (Ca, Pb)₃(PO₄)₅OH solid solution,^{78,79} resulting in significant shifts in diffraction peaks.⁷⁸ However, under our experimental conditions, pure hydroxylpyromorphite was the only mineral phase detected by both GIWAXS and Raman measurements (**Figure 2.1**), and no significant structural incorporation of cations in the hydroxylpyromorphite precipitates was detected. Consistently, zeta potentials of the particles collected from precipitation solutions in the presence of NaNO₃, Ca(NO₃)₂, and Mg(NO₃)₂ (**Table 2.1**, set II) were similar in 4

mM NaNO₃ solution (ξ_w , **Table 2.1**, **Figure A.2**), being -25.2 ± 5.0 , -29.1 ± 1.7 , and -28.1 ± 1.4 mV, respectively.

Size evolutions of precipitates formed in the presence of different cations (set II in **Table 2.1**, 3 mM Na⁺, 1.2 mM Ca²⁺ and Mg²⁺ with the same IS = 4 mM and pH = 7) showed that divalent cations (Ca²⁺ and Mg²⁺) promoted aggregation (**Figure 2.2B**). In the presence of 3 mM NaNO₃, the particle sizes remained unchanged (26 ± 10 nm) within 1 h. In contrast, in the presence of 1.2 mM Ca(NO₃)₂ and Mg(NO₃)₂, the particles grew to 649 ± 26 and 565 ± 24 nm within 1 h. Indicated by the red lines in **Figure 2.2B**, fast initial aggregation occurred in 1.2 mM Ca(NO₃)₂ and Mg(NO₃)₂, similar to $R_{P/Pb} = 1$ solution. SEM observations (**Figures 2.3B** and **Figure 2.3C**) also showed the formation of large aggregates.

Fast aggregation of the precipitates in the presence of divalent cations can be explained by electrostatic interactions. Particles in the precipitation solutions containing Ca²⁺ and Mg²⁺ were only slightly negatively charged, being -12.6 ± 0.6 and -13.3 ± 0.6 mV (ξ_p , **Table 2.1**), which were much less negatively charged than those formed in the presence of Na⁺ ($\xi_p = -39.1 \pm 2.4$ mV). Therefore, only weak electrostatic repulsive forces existed among particles formed in the presence of Ca²⁺ and Mg²⁺, resulting in their fast aggregation.

The mechanisms controlling zeta potential changes (ξ_p , **Table 2.1**, **Figure A.2**) of particles in the precipitation solutions in the presence of Ca²⁺ and Mg²⁺ ions were further explored. The presence of Ca²⁺ and Mg²⁺ ions has been reported to change zeta potentials of various particles (e.g., iron oxide, fullerene, citrate and polyvinylpyrrolidone coated silver particles) by adsorption onto the particle

surfaces.^{80–82} To test potential surface adsorption of Ca^{2+} and Mg^{2+} onto the precipitates, lead phosphate particles were collected from the precipitation solutions (set II, **Table 2.1**) and rinsed with ultrapure water. Then, zeta potentials of the collected particles were measured in both ultrapure water (ξ_w , **Figure A.2**) and in the same salt solutions (ξ_s , **Figure A.2**, 3 mM NaNO_3 , 1.2 mM $\text{Ca}(\text{NO}_3)_2$, and 1.2 mM $\text{Mg}(\text{NO}_3)_2$) of their formation conditions (**Table 2.1**, but without lead or phosphate ions). Surprisingly, zeta potential values of these particles in all salt solutions were similar (ξ_s , **Table 2.1**, being -12.1 ± 1.5 , -5.7 ± 0.5 , and -5.7 ± 0.9 mV in 3 mM NaNO_3 , 1.2 mM $\text{Ca}(\text{NO}_3)_2$, and 1.2 mM $\text{Mg}(\text{NO}_3)_2$ solutions, respectively), and were all similarly less negatively charged than their zeta potentials measured in ultrapure water (ξ_w , **Table 2.1**, -25.2 ± 5.0 , -29.1 ± 1.7 , and -28.1 ± 1.4 mV, respectively). Such measurements suggested that all cations ($\text{Na}^+/\text{Ca}^{2+}/\text{Mg}^{2+}$) adsorbed onto these particles and provided similar extents of charge neutralization.

However, significant differences in zeta potentials of the particles were measured in the precipitation solutions with the remaining lead and phosphate ions (ξ_p , **Table 2.1**, **Figure A.2**), being -39.1 ± 2.4 , -12.6 ± 0.6 , and -13.3 ± 0.6 mV in 3 mM NaNO_3 , 1.2 mM $\text{Ca}(\text{NO}_3)_2$, and 1.2 mM $\text{Mg}(\text{NO}_3)_2$, respectively. Therefore, the presence of lead or phosphate ions must have influenced the adsorption of the cations (Na^+ , Ca^{2+} , and Mg^{2+}) onto the precipitates. Xie et al. reported that the presence of phosphate can promote the adsorption of divalent ion (Pb^{2+}) onto iron oxide particles.⁸³ Here in the precipitation solution containing NaNO_3 , the precipitates were highly negatively charged due to the adsorption of phosphate; in contrast, the precipitates were much less negatively charged in the presence of $\text{Ca}(\text{NO}_3)_2$ and

Mg(NO₃)₂, implying that the presence of phosphate promoted divalent ion (Ca²⁺ and Mg²⁺) adsorption onto the lead phosphate particles, which neutralized the negative zeta potentials of the particles. The Ca²⁺ and Mg²⁺ enrichment on the precipitate surfaces was further confirmed by the chemical composition analysis of the precipitates with ICP-MS, as both Ca/Pb or Mg/Pb ratios in surface layers of the precipitates were higher than those in the inner layers. The detailed information about ICP-MS analysis (**Table A.4**) can be found in the Appendix A.

Lead phosphate aggregation in solutions with varied concentrations of Ca(NO₃)₂ or Mg(NO₃)₂ (**Table A.3** in the Appendix A), typical in water supply systems, was also investigated. With low concentration (0.1 mM) of Ca(NO₃)₂ or Mg(NO₃)₂, no significant aggregation was observed in 1 h. With higher concentrations (0.5 and 0.8 mM) of Ca(NO₃)₂ or Mg(NO₃)₂, significant aggregation of lead phosphate particles was observed, and faster aggregation occurred with higher Ca(NO₃)₂ or Mg(NO₃)₂ concentrations (**Figure A.3**). The observed aggregation trend could also be explained by differences in zeta potentials (**Table A.3** in the Appendix A) of particles formed in precipitation solutions with different cation concentrations. With low Ca(NO₃)₂ or Mg(NO₃)₂ concentration (i.e., 0.1 mM), the zeta potentials of precipitates were measured to be -32.1 ± 1.3 and -33.0 ± 1.6 mV (ξ_p , **Table A.3**), respectively, which were similar to the zeta potentials of the precipitates formed in the presence of NaNO₃ (ξ_p , **Table 2.1**, -39.1 ± 2.4 mV). In comparison, with higher divalent cation concentrations (i.e., 0.5 and 0.8 mM), the particles were much less negatively charged in the presence of Ca(NO₃)₂ (**Table A.3**, ξ_p , -20.8 ± 0.6 and -16.6 ± 0.5 mV) and

Mg(NO₃)₂ (**Table A.3**, ξ_p , -22.7 ± 0.5 and -15.6 ± 1.8 mV), which resulted in less repulsive forces and faster aggregation.

In sum, divalent cations became enriched in the surfaces of lead phosphate particles to neutralize their initially more negative surface charges that were caused by phosphate adsorption and thereby promote their aggregation. The charge neutralization effect is dependent on the concentrations of cations present in solution, and significant aggregation of lead phosphate particles can occur in 1 h with only 0.5 mM Ca(NO₃)₂ or Mg(NO₃)₂.

2.3.3 Structural Incorporation of Anions in Lead Phosphate Particles

Based on GWB calculations (set II, **Table A.2**), all initial solutions containing NaCl, NaF, and NaHCO₃ were supersaturated with respect to hydroxylpyromorphite (SI = 12.6 ± 0.1), Pb₃(PO₄)₂ (SI = 7.3 ± 0.1), PbHPO₄ (SI = 1.6 ± 0.1), and hydrocerussite. The initial solutions were also supersaturated with respect to chloropyromorphite (Pb₅(PO₄)₃Cl, CPM in **Table 2.1**, SI = 24.9), fluoropyromorphite (Pb₅(PO₄)₃F, FPM in **Table 2.1**, SI = 12.3), lead hydroxide (SI = 0.1), and cerussite (SI = 1.2), respectively (**Table 2.1**, set II). In an *in situ* AFM study of the coupled cerussite dissolution and lead phosphate precipitation, Wang et al. found that the anions Cl⁻ and F⁻ substituted for the OH⁻ group in the lead phosphate precipitates, which affected the phase, size, and shape of the precipitates.⁴ Based on GIWAXS and Raman measurements (**Figure 2.1**), the only mineral phases detected were the pyromorphite-group minerals. In the presence of 3.6 mM NaCl, it was hard to identify whether the precipitates were hydroxylpyromorphite or chloropyromorphite by

GIWAXS due to their similar diffraction patterns. In the presence of 3.2 mM NaF, fluoropyromorphite was the only mineral phase detected by GIWAXS. For Raman, the decreased intensity of OH-band ($3550\text{--}3600\text{ cm}^{-1}$) in the presence of 3.6 mM NaCl or 3.2 mM NaF indicated various degrees of channel anion (OH^-) substitution by Cl^- / F^- and the potential formation of chloropyromorphite and fluoropyromorphite.

In solutions with different anions (NO_3^- , Cl^- , HCO_3^- , F^- , set II in **Table 2.1**, **Figure A.4**), sizes of lead phosphate particles were similar ($40 \pm 18\text{ nm}$) with no significant aggregation observed up to 12 days (**Figure A.1**). Zeta potentials of particles formed in all precipitation solutions (set II, ξ_p , **Table 2.1**) were similar and strongly negatively charged, being -39.1 ± 2.4 , -30.7 ± 6.1 , -32.3 ± 1.1 , and $-32.5 \pm 1.8\text{ mV}$ in the presence of NaNO_3 , NaCl , NaHCO_3 , and NaF , respectively, so the strong electrostatic repulsive forces among the particles resulted in their long-term stability. Although fluoropyromorphite and chloropyromorphite formed in the presence of NaF and NaCl , the structural incorporation of varied channel anions in lead phosphate particles did not affect their zeta potentials, resulting in similar aggregation behaviors. Ion substitution in hydroxylpyromorphite has been reported, e.g. Ca-substituted pyromorphites.⁷⁸ Such ion substitution could alter the solubility of lead phosphate precipitates, which could be an interesting future direction.

2.3.4 Retarded Lead Phosphate Aggregation in the Presence of Natural Organic Matter

Previous studies have reported that NOM could adsorb onto various particles (e.g., iron oxide and zinc oxide) and inhibit their aggregation.^{1–3} With high lead concentration (0.5 mM) relevant to the lead-contaminated soil environment, Lang et

al. reported that the presence of NOM decreased the sizes of the chloropyromorphite precipitates, leading to their enhanced mobility in gravel- and sand-packed columns.⁸⁴ To investigate the potential inhibitory effects of NOM on lead phosphate aggregation, experiments with NOM were conducted in a 1.2 mM CaCl₂ solution, as fast aggregation of lead phosphate was observed in 1.2 mM CaCl₂ without NOM (**Figure 2.2C**).

With the addition of small amounts of fulvic acid (0.1 mg C/L), the sizes of lead phosphate particles increased to 581 ± 26 nm in 1 h, which was similar to the sizes in the absence of NOM (with particle size that increased to 544 ± 9 nm in 1 h). However, with the addition of larger amounts of fulvic acid (i.e., 0.5, 2, and 5 mg C/L), the sizes of lead phosphate particles remained constant (49 ± 14 nm) during the 1 h measurements. For the long-term stability of lead phosphate particles in the presence of fulvic acid (**Figure A.1**), slow aggregation occurred in the presence of 0.5 and 2 mg C/L fulvic acid, and particle sizes increased to 415 ± 47 and 410 ± 73 nm after 1 day. However, in the presence of 5 mg C/L fulvic acid, the sizes of lead phosphate particles remained unchanged for 12 days. In summary, fulvic acid significantly inhibited the aggregation of lead phosphate particles, and the inhibitory effects correlated with the concentrations of fulvic acid.

Size evolution of lead phosphate particles was also measured in a 1.2 mM CaCl₂ solution in the presence of humic acid with four different concentrations (0.05, 0.1, 0.5 and 5 mg C/L). In the presence of low concentrations of humic acid (0.05 and 0.1 mg C/L humic acid), the sizes of lead phosphate particles increased to 304 ± 15 and 202 ± 12 nm in 1 h. However, with high concentrations of humic acid (i.e., 0.5

and 5 mg C/L), the sizes of lead phosphate particles remained constant (68 ± 31 nm) during the 1-h measurements. Therefore, similar to fulvic acid, humic acid retarded the aggregation of lead phosphate particles, and the retardation effect correlated with the concentrations of humic acid.

To explain the observed aggregation behaviors, zeta potentials of lead phosphate particles in a CaCl_2 precipitation solution were compared in the presence and absence of NOM (set III, **Table 2.1**). In the presence of 0, 0.1, 0.5, 2, 5 mg C/L fulvic acid, the zeta potentials (ζ_p , **Table 2.1**) of lead phosphate particles in the precipitation solutions were -13.4 ± 0.5 , -14.4 ± 1.7 , -16.6 ± 0.7 , -18.0 ± 0.5 , and -19.3 ± 1.0 mV, respectively. In the presence of 0, 0.05, 0.1, 0.5, and 5 mg C/L humic acid, the zeta potentials (ζ_p , **Table 2.1**) of lead phosphate particles in the precipitation solutions were -13.4 ± 0.5 , -15.6 ± 1.3 , -15.9 ± 0.9 , -16.4 ± 0.6 and -18.3 ± 0.4 mV, respectively. The lead phosphate particles were slightly more negatively charged in the CaCl_2 precipitation solution in the presence of NOM, resulting in stronger electrostatic repulsion forces among particles and thus slower aggregation. In previous studies, the presence of NOM has been reported to result in more negative zeta potentials of iron oxide particles at neutral pH conditions (pH 7.2), due to the adsorption of deprotonated NOM onto the particles.⁵⁵ Previous studies of iron oxide aggregation also suggested the increased steric repulsive forces among particles in the presence of NOM.^{2,85,86} Here steric repulsion among lead phosphate particles due to NOM adsorption could have also contributed significantly to the inhibitory effects of NOM on aggregation, especially considering the small changes in zeta potentials of particles in the presence and absence of NOM.

2.3.5 Promoted Lead Phosphate Aggregation under High Ionic Strength

Size evolution of lead phosphate particles in solutions with different ionic strength values (IS, set IV in **Table 2.1**) is shown in **Figure 2.2D**. During the 1-h measurements, under high IS (i.e., 30, 50, 80 and 99 mM), the lead phosphate particles grew rapidly from 40 ± 18 nm to 74 ± 10 , 414 ± 22 , 515 ± 17 , and 689 ± 18 nm. In contrast, the particle sizes (40 ± 18 nm) were relatively constant under low IS (i.e., 0.58, 4, 11 and 21 mM) in 1 h. For long-term size measurements in solutions with low IS, no aggregation occurred for 12 days in solutions with IS = 0.58, 4, and 11 mM. However, the lead phosphate particles under IS = 21 mM started to aggregate after 3 days, with sizes increasing to 168 ± 20 nm (**Figure A.1** in the Appendix A).

The promotion of aggregation at higher IS could be explained well by the electrostatic interactions among particles according to DLVO theory.⁸⁷ The electrostatic repulsion energy (V_{EDL}) among particles could be affected by both the zeta potentials of the particles (ξ) and the Debye length (κ^{-1}). The zeta potential values of particles in precipitation solutions with varied IS (0.58, 4, 11, 21, 30, 50, 80, and 99 mM) were similar, being -43.7 ± 1.5 , -39.1 ± 2.4 , -40.1 ± 1.3 , -34.8 ± 1.2 , -38.2 ± 1.6 , -37.7 ± 3.4 , -38.9 ± 1.0 , and -37.3 ± 2.2 mV (ξ_p , **Table 2.1**), respectively. Under higher IS, the electrical double layers among particles were compressed, leading to smaller Debye length, which could result in decreased electrostatic repulsion energy (V_{EDL}) among particles, thus promoting their aggregation.

As required by EPA, total dissolved solids in drinking water should be lower than 500 mg/L.⁸⁸ Thus, the IS values in the drinking water supply system are typically below 10 mM. Based on our results, aggregation of lead phosphate particles in a

drinking water supply system with $IS < 10$ mM would not occur within 12 days, because the excess phosphate (as $R_{P/Pb} = 100$ in set IV) would stabilize the particles. The formation of small lead phosphate particles with long-term stability in suspension may explain the reported high total lead concentrations in tap water after phosphate addition for months at D.C. and Flint, as well as in the pilot-scale pipe-loop studies.^{49,50,52,53}

2.3.6 Lead Phosphate Particles with High Stability under pH 5.5-8.5

GWB calculation (**Table A.2**) showed that under pH 8.5, the solution was saturated with respect to lead hydroxide ($SI = 1.4$), cerussite ($SI = 1.2$) and hydrocerussite ($SI = 4.4$). However, both Raman and GIWAXS measurements only detected the formation of hydroxylpyromorphite under all pH conditions (**Figure 2.1**).

Figure A.5 presents size evolution of particles precipitated under three different pH conditions (5.5, 7.0 and 8.5). Within 1 h, the particle sizes remained constant, being 65 ± 22 , 40 ± 18 , and 62 ± 26 nm at pH = 5.5, 7.0, and 8.5, respectively. This is because the particles that formed in the precipitation solutions (set V in **Table 2.1**) were all highly negatively charged, with zeta potentials (ζ_p , **Table 2.1**) of -38.7 ± 1.0 , -39.1 ± 2.4 and -27.3 ± 3.4 mV at pH 5.5, 7.0, and 8.5, respectively. This explains why particulate lead could remain in high levels in tap water. More detailed discussion of the pH effects on zeta potentials and mineral formation is available in the Appendix A.

2.4 Conclusions

Lead release from pipes and fittings in supply systems is a serious threat to public health. Due to low solubility of lead phosphate, phosphate addition has been widely used to reduce lead concentrations in tap water. However, the total lead concentrations in tap water for several water systems have been observed to remain high for several months after phosphate addition. It is possible that dissolved lead concentrations decrease rapidly as lead phosphate forms but that elevated total lead concentrations persist because of the stability of lead phosphates as particles in suspension. In pilot-scale pipe studies, the lowest total lead concentration in water was not achieved with the highest amount of phosphate addition.⁵³ These previous observations suggested the important roles of particulate lead transport in pipes that are now supported by observations from the current study.

Particulate lead transport is controlled by deposition, which can be affected by aggregation. Here, lead phosphate formation and aggregation were studied under varied aqueous conditions typical in water supply systems. Aggregation of lead phosphate particles was found to be mainly controlled by zeta potentials, which can be affected by the adsorption of excess phosphate ions, divalent cations, and NOM, and not affected much by the presence of anions, the pH conditions investigated here (5.5-8.5), and the ionic strength typical in drinking water systems. pH probably has an effect on aggregation of lead phosphate particles but the effect would not be manifested over the range of pH values for drinking water systems. In addition, enhanced steric repulsive forces by NOM also played a crucial role. Although the addition of excess amounts of phosphate can promote the formation of lead phosphate

particles and lower dissolved lead concentration, it could increase the stability of lead phosphate particles, resulting in high particulate lead concentration in tap water. Thus, it is vital to determine an optimal phosphate dosage for lead immobilization in lead pipes. Furthermore, overdosed phosphate can cause eutrophication problems if the phosphate is not adequately removed from the water before it is discharged back to the environment.⁸⁹ The presence of Ca^{2+} and Mg^{2+} at concentrations of 0.5 mM or higher promoted the aggregation of lead phosphate particles within 1 hr, which are at levels that are below the 500 mg/L total dissolved solids concentration required for drinking water.⁸⁸ In the US, the divalent cation concentrations in drinking water range from very low concentrations to nearly 5 mM for calcium and 2 mM for magnesium.^{90,91} For sites with Ca and Mg concentrations larger than 0.5 mM, fast aggregation of lead phosphate particles is expected, suggesting effective total lead removal through phosphate addition. Our findings also suggest that while considering hardness control, it would be beneficial to have some amounts of divalent cations in drinking water distributed through lead pipes, to promote particulate lead removal after phosphate addition. The concentrations of NOM were found to correlate with their retardation effects on lead phosphate aggregation. Therefore, when considering the effects of NOM on drinking water quality, issues of the stability of lead phosphate stability in addition to the formation of disinfection byproducts should be considered.

This study focused on systems for which Pb(II) minerals, either carbonates or phosphates, would be the dominant constituents of lead-containing scales and suspended particles. Studying effects of disinfectants which might change the oxidation state of lead-containing particles could be an interesting future direction. This study

provides fundamental nanoscale understanding of lead phosphate aggregation, bench-scale and pilot-scale pipe loop studies are needed to verify the effects of aggregation on deposition of particulate lead onto pipe walls.

CHAPTER 3. LEAD PHOSPHATE DEPOSITION IN POROUS MEDIA: IMPLICATIONS FOR LEAD REMEDIATION IN SOILS

3.1 Introduction

Lead contamination in soil has been a world-wise issue which attracts much attention, and lead exposure through soil has been regarded as an important pathway.⁹² Exposure to lead in soil causes a series of health impacts, including neurological impairment and defects in immune and urinary system,^{93,94} and children and pregnant women are the most likely to be affected.⁹⁵

Compared to excavating contaminated soil and refilling with clean soil, in situ remediation is less expensive, more efficient and more sustainable.^{96,97} In situ chemical immobilization methods include the use of lime and cement as a stabilization/solidification technique, forming insoluble lead hydroxides ($K_{SP} = 1.2 \times 10^{-15}$).⁹⁸ Alternatively, phosphate addition is widely adopted to immobilize lead in soil due to formation of lead phosphates with even lower solubility, especially pyromorphites (e.g., for hydroxylpyromorphite, $K_{SP} = 10^{-76.8}$).⁹⁹ By forming lead phosphate particles after adding phosphate, dissolved lead concentrations could be lowered significantly under acidic to neutral pH, indicating that release of dissolved lead can be effectively controlled.⁹⁶ However, the lead phosphate particles can still pose a risk to water supplies if they are mobile in the soil. The aggregation state of lead phosphate particles, as well as the interactions among aqueous species, soil, and lead phosphate particles, might affect their deposition onto soil, thus impacting their fate and transport in porous media.

The effects of water chemistry parameters (e.g., NOM and Cl^- , F^-) on the formation of lead phosphate particles has been studied by a few researchers.^{4,84} These studies mainly focused on change in size and phase of lead phosphates formed in response to change in certain parameters. For example, Wang et al. found that Cl^- and F^- substitution for OH^- of lead phosphates altered particle size and morphology by using atomic force microscopy (AFM), which was in line with change in mineral phase detected by Raman spectroscopy.⁴ Lang et al. reported that the presence of NOM reduced the size of chloropyromorphite, and their mobility in sand columns was enhanced accordingly.⁸⁴ Our previous work also investigated effect of aqueous parameters on aggregation of lead phosphate particles in water supply systems.¹⁰⁰ However, effects of these parameters on the deposition behavior of lead phosphate particles has not been systematically studied.

The water chemistry, including pH, ionic strength (IS), and presence of cations, is known to influence the aggregation and deposition of particles in porous media by modifying the surface charge state of the particles and collectors or screening charges; the presence of natural organic matter (NOM) or polymers can further block deposition sites or induce either bridging or steric repulsion between the particles and collectors.^{87,101–105} These previous studies can shed some light on particulate lead transport in soils; however, to best of our knowledge, few studies have investigated the transport of particulate lead. Although deposition of engineered nanoparticles has been extensively investigated, studies on deposition of such “naturally formed” particles is scarce. Butkus et al. stated that $\text{PO}_{4(\text{aq})}$ amendment substantially reduced mobility of both forms of particulate lead ($\text{Pb}_{(\text{aq})}$ and PbO), according to column

experiment results.¹⁰⁶ They also predicted attachment of lead-containing particles (PbO and $\text{Pb}_3(\text{CO}_3)_2\text{OH}_2$) to porous media with the aid of Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. However, predicting transport of other particulate lead, especially lead-phosphate species, remains to be explored. To parameterize these models, the Hamaker constant of the lead phosphate particles is needed, which has not been reported elsewhere. It has also not yet been determined whether standard clean bed filtration models and DLVO theory (accounting for van der Waals and electrostatic interactions) will be successful to predict the measured particle deposition behavior, as evaluated by colloid filtration theory (CFT) across a variety of conditions. Mechanistic studies are needed that identify the relevant collision and attachment interactions involved in the particle deposition to assess whether standard clean bed filtration theory is applicable or whether extensions to the model would be required.

The objectives of this study are two-fold: (1) to investigate the effect of various aqueous parameters (IS, P/Pb ratios, as well as the presence of divalent cations (Ca^{2+}), and NOM (humic acids)) on the deposition of lead phosphate particles; and (2) compare DLVO predictions to empirical results from column experiments to assess the suitability of clean bed filtration theory to predict the deposition behavior of lead phosphate particles purely from the particle/collector properties and homoaggregation behavior of the lead phosphate particles. Dynamic light scattering (DLS) was employed to record the size evolution of lead phosphate particles to calculate aggregation rates and Hamaker constant. Column experiments were conducted, and lead concentrations in effluents and sand columns were measured by flame atomic absorption spectroscopy (FAAS). Empirical attachment efficiencies (α) were

determined in response to ionic strength using colloid filtration theory (CFT), and these results were compared to predictions using standard DLVO theory for clean-bed filtration (i.e., assuming only particle-clean substrate interactions). The new knowledge obtained in this study can help optimize lead immobilization strategies in soils.

3.2 Materials and Methods

3.2.1 Lead Phosphate Preparation

Stock solutions of 10 mM $\text{Pb}(\text{NO}_3)_2$ (ACS reagent, $\geq 99.0\%$, Sigma-Aldrich, St. Louis, MO), 100 mM Na_2HPO_4 (99+ %, Acros Organics, Morris Plains, NJ), 100 mM NaH_2PO_4 (99%, Acros Organics, Morris Plains, NJ), 1 M NaNO_3 (ACS reagent, $\geq 99.0\%$, Sigma-Aldrich, St. Louis, MO), and 10 mM $\text{Ca}(\text{NO}_3)_2$ (from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, ACS reagent, 99+%, Acros Organics, Morris Plains, NJ) were prepared using CO_2 -saturated ultrapure water (resistivity $> 18 \text{ m}\Omega$). Humic acid (technical grade, Sigma-Aldrich, St. Louis, MO) stock solutions were also prepared at 3 g in 250 mL and filtered, then measured by total organic carbon (TOC) analysis as described in the Appendix B. Then, stock solutions were diluted and mixed to prepare solutions (**Table 3.1**) for lead phosphate particle formation through aqueous precipitation. Na_2HPO_4 and NaH_2PO_4 were used as both the phosphate source and the buffer to maintain $\text{pH} = 7.0 \pm 0.1$. NaNO_3 was used to adjust ionic strength of solutions. Four sets of experiments were conducted to investigate effects of ionic strength (5, 10, 12.5, 15, and 20 mM, set I), total P/Pb ratios ($R_{\text{P/Pb}} = 10$ and 1, set II), divalent cation (0.2 and 1 mM Ca^{2+} , set III), and NOM (0.05 and 5 mg C/L of humic

acid, set IV) on the deposition of lead phosphate particles. During phosphate amendments for lead immobilization in soil, $R_{P/Pb} \approx 4$ was commonly adopted.^{107–109} Here, $R_{P/Pb} = 10$ was selected for all experiments except those designed to study the effect of P/Pb ratios (set II). Na_2HPO_4 and NaH_2PO_4 solutions were first mixed with salt solution ($NaNO_3$ or $Ca(NO_3)_2$) or NOM (humic acid), and the mixture was vortexed for 5 s. Then $Pb(NO_3)_2$ was added, and lead phosphate precipitation started promptly. All experimental conditions, including pH and IS, were calculated using Minteq database in Geochemist's Workbench (GWB, student version 11.0) (**Table 3.1**).

Table 3.1. Initial experimental conditions for lead phosphate precipitation (pH = 7.0)^b

Set	$R_{P/Pb}$	Pb, mM ^a	P, mM ^a	NO ₃ ⁻ , mM	Na ⁺ , mM	Ca ²⁺ , mM	IS, mM ^b	
Aggregation experiments for CCC and CDC determination								
IS 2 – 500 mM	10	0.10	1.00	0.20	1.50		2	
		–	–	–	–	-	–	
		0.48	4.80	520.20	527.90		500	
Deposition experiments								
I	IS-5 – 20 mM	10	0.10	1.00	3.20	4.49		5
			–	–	–	–	-	–
			0.12	1.20	18.20	19.86		20
II	$R_{P/Pb} = 1$	1	0.22	0.22	9.36	9.37	-	10
III	0.2 mM Ca(NO ₃) ₂	10	0.10	1.00	8.20	9.19	0.2	10
	1 mM Ca(NO ₃) ₂		0.10	1.00	7.20	6.62	1	
IV ^f	0.05 mg C/L HA	10	0.10	1.00	8.20	9.19	0.2	10
	5 mg C/L HA							

Note: ^aPb and P: calculated total lead and phosphate concentrations, which were consistent with measurements using ICP-MS. ^bIS (Ionic Strength) and pH were

calculated using GWB based on initial solution conditions. Conductivity and pH were measured at the beginning and end of the column experiments, and no significant differences were observed.

3.2.2 Dynamic Light Scattering (DLS) and Zeta Potential Measurements

Precipitation solution was freshly prepared (**Table 3.1**). After vortexing for 5 s, 1 mL of the precipitation solution was added to a cuvette (ZEN0040, Malvern Panalytical, Malvern, UK) and measured on a Zetasizer Nano ZSP instrument (Malvern Panalytical, Malvern, UK). For homoaggregation experiments, the size evolution was monitored consecutively for 1 h. The *z*-average diameter was presented. At the end of size measurements, the cuvette was equipped with a dip cell (ZEN1002, Malvern Panalytical, Malvern, UK) and the zeta potential of the lead phosphate particles was measured. To explain the deposition behaviors of lead phosphate particles in fresh and aged suspensions (described in the following sections), similarly, 1 mL of freshly prepared precipitation solution was injected to cuvette, and the size of lead phosphate particles was measured after 15 min and 21 h.

To understand interactions between particles and sand collectors, the zeta potentials of sand in the various background solutions (similar components to precipitation solution, excluding $\text{Pb}(\text{NO}_3)_2$, **Table 3.1**) were also measured. Crushed sand was added to background solution and the mixture was vortexed for 5 s. After settling for 1 h, 1 mL of the colloidal suspension was taken from the top layer of the mixture and transferred to a cuvette equipped with a dip cell for zeta potential measurements. Triplicate experiments were performed, and the average and standard deviation values are listed in **Table 3.1**.

3.2.3 Sand Column Preparation and Characterization

A glass chromatographic column (20 cm length, 1.0 cm inner diameter) with an upper end cap (2.5 cm length, 1.5 cm inner diameter) (Kimble FLEX-COLUMN, DWK Life Sciences, Milville, NJ) was packed with Ottawa sand (VWR, Solon, OH) using a wet packing method. Nylon mesh (150 μm Nitex, Sefar, Buffalo, NY) was attached to the ends of the column to prevent loss of sand. Details are in the Appendix B. To determine the hydrological parameters of the packed porous media, a tracer experiment using NaBr was conducted. 10 pore volumes (PVs; 1 PV = 8 mL) of NaBr solution were injected at a flow rate of 1 mL/min (linear velocity of 3.2 cm/min or 4.6 m/d), followed by introduction of 6 PVs of ultrapure water, and Br^- concentrations in the eluent fractions were measured by a bromide ion-selective electrode (Cole-Parmer, Vernon Hills, IL). The elution of the step input profile of the NaBr breakthrough curve was fitted using the CXTFIT model (STANMOD Suite v. 2.08) to estimate the dispersivity, with both the dimensionless velocity and retardation factor fixed at 1, and reaction or deposition fixed at 0 (**Figure B.1**).

3.2.4 Lead Phosphate Deposition Experiments

The homoaggregation experiments on the lead phosphate particles under varying IS (5 - 20 mM, **Figure 3.1**) demonstrated that the size of the particles increased distinctly over 1 h at higher IS ≥ 12.5 mM. Although aggregation state has been reported to not essentially change the strength of the colloidal interaction between particles and collectors (i.e., the attachment efficiency), it may still change the deposition behavior by affecting the hydrodynamics of transport.¹¹⁰ Therefore,

both fresh and aged (21 h) suspensions were compared in deposition experiments. After preparation (**Table 3.1**), the suspension was injected (fresh suspension: immediately after preparation, aged suspension: left sitting for 21 h) into the pre-packed sand column for lead phosphate deposition tests. Prior to each experiment, the packed column was flushed with 8 PVs of background solution (similar components to precipitation solution, excluding $\text{Pb}(\text{NO}_3)_2$, **Table 3.1**). Then, 10 PVs of precipitation solution (phase I), followed by 6 PVs of background solution (phase II), were injected to the column in the up-flow direction using a syringe pump (flow rate of 1 mL/min or linear velocity of). 16 PVs of effluent were collected continuously. For each pore volume of effluent, 4 mL was filtered using a 0.1 μm PVDF syringe filter (Durapore, Merck Millipore, Carrigtwohill Co., Cork, Ireland), then the filtered sample was digested overnight by adding concentrated nitric acid (67-70%, TraceMetal grade, Fisher Scientific, Waltham, MA) to a final concentration of 2% nitric acid, for concentration measurement of the $< 0.1 \mu\text{m}$ Pb (dissolved lead or small nanoparticles) by flame atomic absorption spectroscopy (FAAS) (AAAnalyst 200, PerkinElmer, Waltham, MA). The other 4 mL of effluent was directly treated with nitric acid for total Pb concentration measurement. Simulated breakthrough curves were fitted using CXTFIT with a fixed dimensionless velocity of 1 PV/RT and dimensionless dispersion number (i.e., $1/\text{Pe}$) of 0.143 determined in a NaBr tracer test. The breakthrough curve at 5 mM was fitted for both the retardation factor ($R = 1.2$) and deposition coefficient μ , and R was held fixed at 1.2 and μ fitted for all other conditions. For cases showing ripening, the breakthrough curve is fitted through only the initial data points to extrapolate an estimate of C/C_0 without ripening. Column

experiments data was collected and processed by Juntao Zhao, and CXTFIT fitting was performed by Daniel Bao.

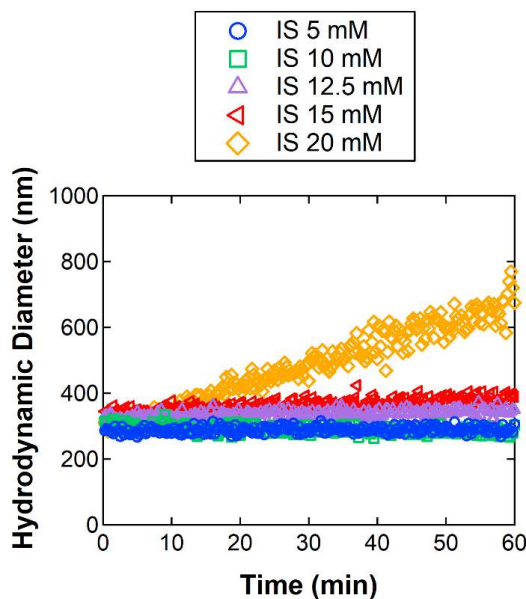


Figure 3.1. Size evolution of lead phosphate particles formed under IS 5 to 20 mM within 1 h as measured by DLS.

To quantify Pb retention within the column at the end of deposition experiments, liquid residual was separated from the column by collecting liquid that drained from the inlet of the column with manual shaking to dislodge the liquid, and digesting the liquid using 2% HNO_3 matrix overnight. The volume of liquid residual collected in each experiment was recorded for mass balance calculations. Then, the sand was extruded, and divided into 10 sections along the column length. The mass of each section was measured and recorded. Then, each section was digested with 5 mL of 2% nitric acid overnight before chemical analysis. Finally, the residual sand after extrusion was rinsed off the sides of the column walls with 5 mL of 2% HNO_3 and

allowed to soak overnight to include in mass balance calculations for total lead recovery.

3.3 Results and Discussion

3.3.1 Behavior of Lead Phosphate Particles in Monovalent Electrolyte (NaNO₃)

3.3.1.1 Precipitation and Homoaggregation of Lead Phosphate Particles at Varied Ionic Strength

The homoaggregation behavior of particles was measured under a wide range of ionic strengths (IS) of 2 mM to 200 mM by adding NaNO₃ (**Figure B.2a**), and the attachment efficiency as a function of IS was plotted (**Figure B.2b**). The critical coagulation concentration (CCC) for the lead phosphate particles was estimated to be 99 mM. Interestingly, the zeta potential of the precipitates was similar across the range of IS up to the CCC, which is atypical of charge screening of a particle with constant surface charge as would be predicted by Gouy-Chapman theory. The results would suggest a higher surface charge develops (e.g. by phosphate adsorption or incorporation) in the higher IS conditions. The measured zeta potentials under the varied IS (**Figure B.3**) were used to parameterize the DLVO model (Equations B.4 to B.7, Appendix B) and compute interaction energy profiles. Assuming that at the CCC, there should be no energy barrier to attachment, the Hamaker constant of the lead phosphate particles in water was estimated as that resulting in $V_T(h) \leq 0$ at all distances $h > 0$, being 3.0×10^{-20} J at the CCC of ≈ 100 mM IS (**Figure B.4**). It is noted that some uncertainty exists in this analysis, in that a secondary energy minimum is observed in the DLVO

profiles in which the particles could agglomerate; if this process is also considered, the estimated Hamaker constant would be lower. However, the estimated value of 3.0×10^{-20} J is of a reasonable order of magnitude relative to Hamaker constants reported for other inorganic materials.¹¹¹

3.3.1.2 “Freshly-Prepared” Lead Phosphate Particles Show Ripening in Column Deposition Experiments with Monovalent Electrolyte (NaNO₃)

Column experiments were performed over a narrower range of IS (5, 10, 12.5, 15, and 20 mM) across which nearly complete to nearly zero breakthrough was observed. Additional homoaggregation studies were hence conducted to monitor aggregation at these IS over 60 min, as a relevant timeframe for the column deposition studies. Because slow aggregation was observed in this ionic strength range, column experiments were run with both fresh suspensions (prepared immediately before introduction to the column) and aged suspensions (prepared 21 h before introduction to the column) to investigate the influence of the initial aggregation state. Correspondingly, the particle size was also measured after 15 min and 21 h aging of the suspension (**Figure 3.2b**). Increasing aggregation was apparent with increasing ionic strength, with a significant proportion of large agglomerates observed at 12.5 mM IS and higher after 21 h. Effluent from the columns was measured for total lead (unfiltered) (**Figure 3.3**) and the $< 0.1 \mu\text{m}$ lead (**Figure B.5a**, and **Figure B.5c** for the computed $> 0.1 \mu\text{m}$ lead). The $< 0.1 \mu\text{m}$ lead was generally low except at the lowest ionic strengths, where small unaggregated nanoparticles may be able to pass the filter. Hence, results

are discussed for the total lead breakthrough, while the breakthrough profiles of > 0.1 μm show largely the same trends.

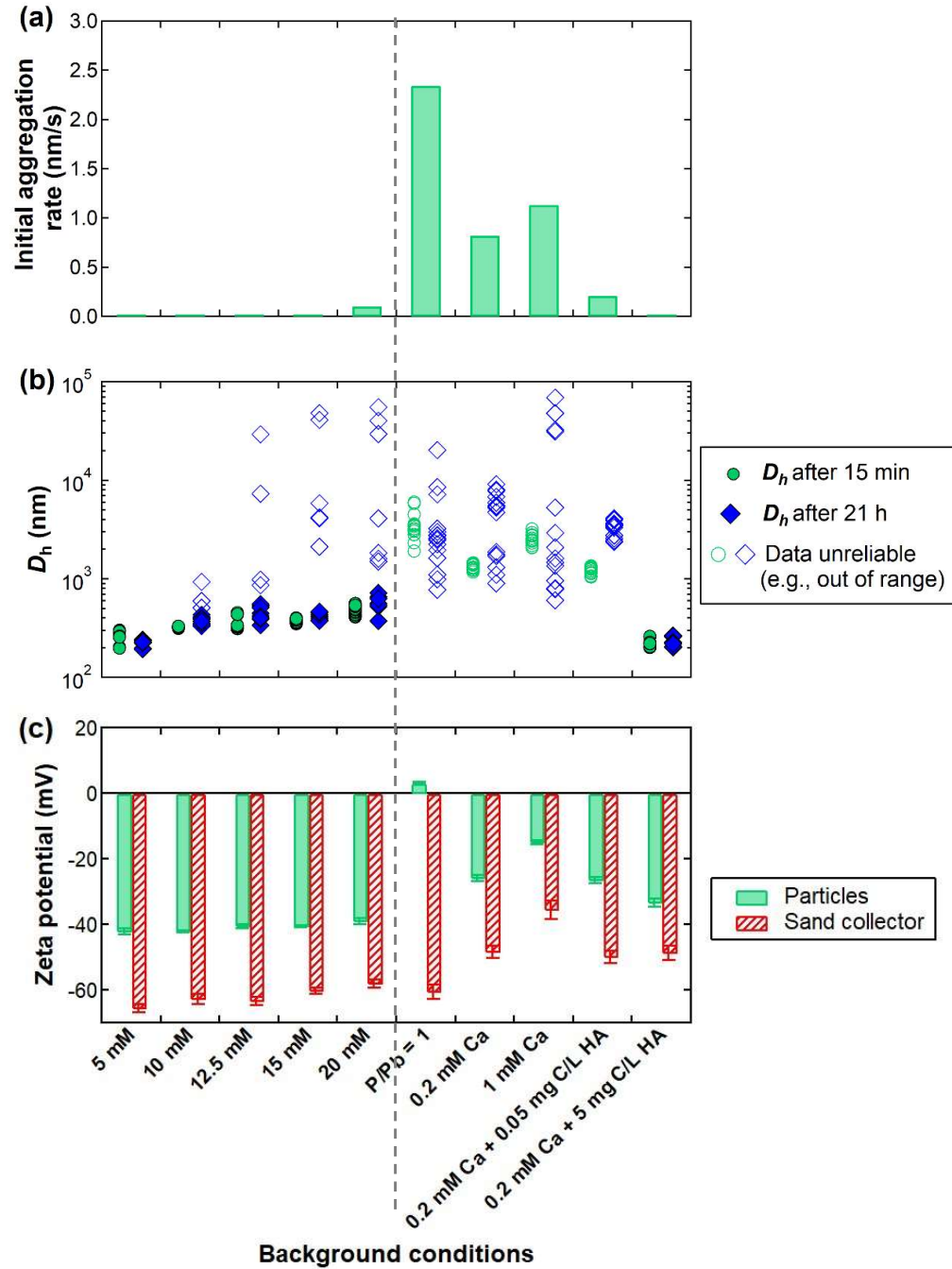


Figure 3.2. Initial aggregation rates of the lead phosphate particles (a), z -average particle diameters after 15 min and 21 h (b), and zeta potentials of lead phosphate particles and sand collectors (c).

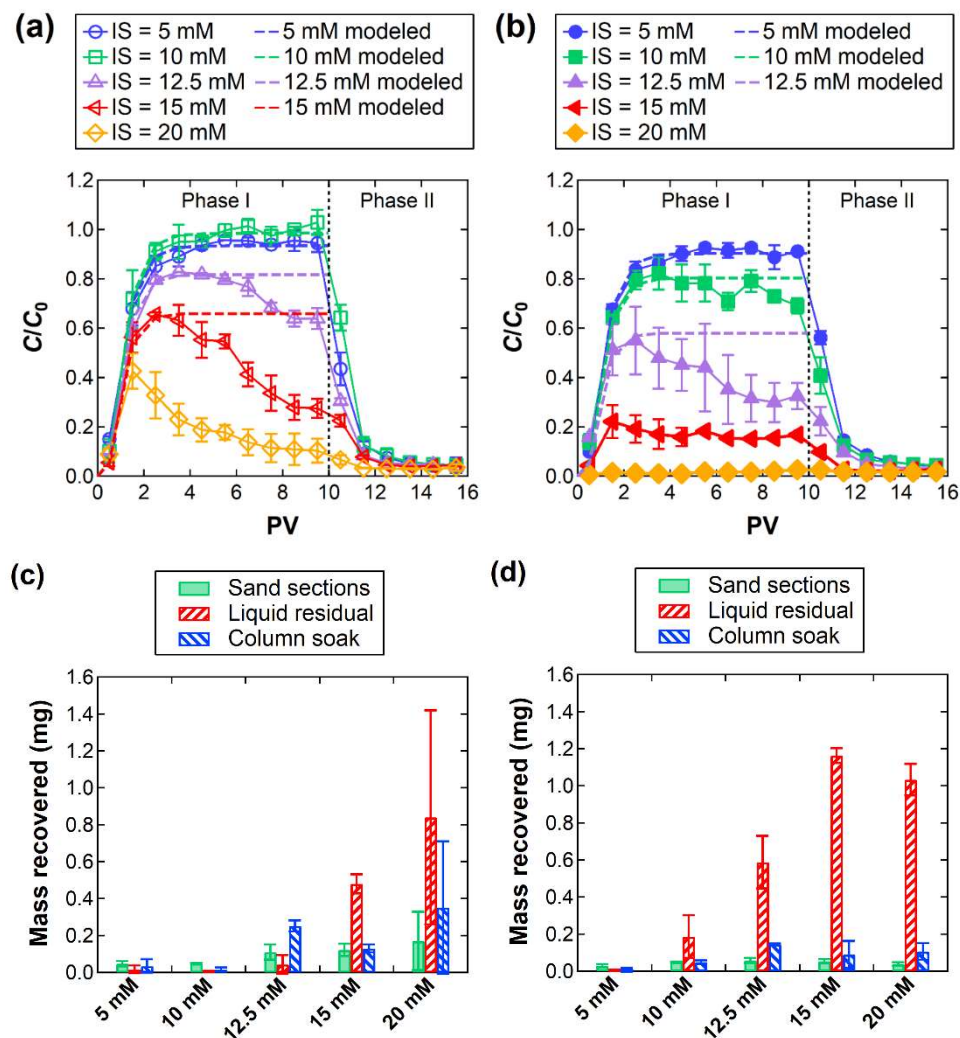


Figure 3.3. Breakthrough curves of total lead under IS 5-20 mM and fitting results using CXTFIT for fresh suspensions (a) and aged suspensions (b) of lead phosphate particles, and lead mass recovered for fresh (c) and aged (d) suspensions.

For fresh suspensions under low ionic strength (5 and 10 mM), lead started to present in the effluent from the first PV and consistently increased to a high plateau recovery rate (C/C_0) of total lead (0.95 and 1.00, respectively) during phase I (**Figure 3.3a**). After switching to lead-free background solution (starting from PV 11), the concentration of lead phosphate in the effluent rapidly declined, suggesting minimal detachment of the previously deposited lead. The retention profiles and mass recovery

analysis after sectioning the column also showed minimal deposition in the column (**Figure B.6a** and **Figure 3.3c**). The recoveries from the mass balance were also computed, which can be found in Appendix B (**Figure B.7**). The shape of the breakthrough curves at 5 and 10 mM could be fitted well with CXTFIT modeling (**Figure 3.3a**), suggesting typical clean bed filtration behavior.

In contrast, at higher ionic strengths (12.5 and 20 mM), the breakthrough curves showed an initial increase in effluent lead followed by declining recovery over time, with the ultimate recovery rate of total lead after 10 PVs of injection declining to ≈ 0.10 under 20 mM ionic strength (**Figure 3.3a**). Correspondingly, lead mass recovered from the column was higher at higher ionic strength, with high proportion of lead found in the liquid residual (**Figure 3.3c**) which indicated particles were weakly attached to sand collectors and thereby easily transferred to liquid as a result of the manual shaking. These observations suggest a ripening phenomenon occurred, during which particles attach to those already deposited to collectors.^{112,113} Hence, the breakthrough curves are not amenable to fitting by clean-bed filtration theory. To better visualize the degree of ripening, breakthrough curves were extrapolated by fitting the initial increasing portion of the breakthrough curve to provide an estimate of a predicted plateau C/C_0 if no ripening occurred (**Figure 3.3a**). A higher extent of ripening is observed at 20 mM IS compared to 12.5 mM IS. The retention profile in the sand column (**Figure B.6a**) shows that nearly all deposited lead is found near the column inlet. Interestingly, at higher IS, particularly 15 and 20 mM, the mass of lead recovered from the sectioned sand (denoted “sand” in **Figure 3.3c**) was low, whereas most of the lead was recovered in the liquid residual (denoted “residual”) and to some

extent, in the HNO₃ soak of the column and remaining sand after column sectioning (denoted “soak”). The high proportion of lead in the liquid residual suggests that strong attachment onto the sand substrate did not occur under these cases, and the results can instead be consistent with ripening to form loose aggregates of lead phosphate particles extending into the liquid phase that are only weakly attached to the sand.

The influence of ripening can appear remarkable given that the measured homoaggregation was slow, particularly at 12.5 and 15 mM IS (**Figure 3.1** and **Figure 3.2**). To explain these results, the rate of particle-particle collisions (including those that do not result in attachment) was estimated in the homoaggregation samples using Smoluchowski theory,¹¹⁴ versus the rate of particle-collector collisions in the deposition experiments.¹¹⁵ The particle-particle collision rate (in suspension) is estimated to be $1.3 \times 10^{12} \text{ m}^{-3} \text{ s}^{-1}$ on a per volume basis (or $1.3 \times 10^6 \text{ s}^{-1}$ in the 1 mL DLS sample volume), whereas the particle-collector collision rate was estimated to be orders of magnitude higher at $3.5 \times 10^{15} \text{ m}^{-3} \text{ s}^{-1}$ (or $7.0 \times 10^{10} \text{ s}^{-1}$ in the 20 mL column volume). Hence, the magnified influence of ripening in the deposition studies relative to aggregation in the homoaggregation studies can be consistent with the higher rate of interaction with sand collectors and any previously deposited particles.

3.3.1.3 “Aged” Lead Phosphate Particles Show Straining in Column Deposition Experiments with Monovalent Electrolyte (NaNO₃)

Breakthrough curves from aged suspensions showed similar trends to the fresh suspensions. However, under higher IS (10 to 20 mM), breakthrough curves from aged

suspensions were dramatically lower than those from fresh suspensions. According to DLS results, long-term aggregation was negligible at 5 mM IS (particle diameter remained at 219 ± 19 nm after 21 h, compared to 251 ± 41 nm after 15 min), while increasingly large aggregates were observed in 10, 12.5, 15, and 20 mM IS when considering all individual measurements (five measurement replicates per sample $\times$ triplicate sample preparations). For the 10, 12.5, 15, and 20 mM samples, the sizes measured in the first one to two measurement replicates per sample were typically larger than the following replicates, suggesting the existence of both small and large (e.g. > 1 μm diameter) aggregates, with the large aggregates settling outside the measurement window over time.

A prior theoretical and experimental study on the deposition behavior of aggregates suggested that the attachment efficiency α representative of the energy barrier to particle-substrate attachment should not depend strongly on the particle aggregation state, as the bulk of the aggregate does not approach closely to the substrate surface.¹¹⁰ Hence, the significant enhancement in deposition of the aged lead phosphate suspensions suggests that straining occurred, in addition to the deposition and ripening phenomena observed in the freshly prepared suspensions. The results are consistent with the expectation that straining can occur when the ratio of particle to collector size lies between approximately 0.002 and 0.15.^{116,117} In this study, the average diameter of the 30-40 mesh Ottawa sand collectors was 507.5 μm . Therefore, the range of particle size to induce straining was calculated to be from 1015 to 76125 nm, consistent with the presence of large aggregates observed after 21 h in IS ≥ 12.5 mM and, to a lesser but observable extent, in 10 mM IS (**Figure 3.2b**). As for the

freshly prepared suspensions, a predominance of lead in the liquid residual is apparent for the aged suspensions even at 10 mM IS (**Figure 3.3d**), also consistent with a straining mechanism whereby particles are physically strained in the pores as opposed to strongly attached onto the sand substrate.

3.3.1.4 DLVO Modeling Suggests Lead Phosphate Particle Deposition in Monovalent Electrolyte is Also Attributable to Deposition in the Secondary Minimum

Standard DLVO theory accounts for van der Waals and electrostatic interactions and can hypothetically be used to model particle-substrate interaction energy profiles, given the properties of the lead phosphate particles and sand collectors. The critical deposition concentration (CDC) can be estimated as the ionic strength where no energy barrier to deposition occurs. Given the clear existence of ripening and straining phenomena, DLVO theory accounting only for clean-bed deposition is not expected to apply when particle-particle attachment is also occurring. However, the DLVO prediction can still be useful for environments with lower lead concentrations where particle-particle interactions leading to ripening and straining will be less likely to occur, or during the early stage of breakthrough where the sand bed is indeed “clean.” Therefore, we explored whether theoretical DLVO calculations could predict early-stage particle breakthrough behavior before the onset of extensive ripening.

To parameterize the DLVO model, the zeta potentials of the particles were measured at all IS used in the deposition experiments as well as higher IS up to 500 mM. The zeta potentials of colloidal particles from the Ottawa sand were also

measured (**Figure 3.3c**). The Hamaker constant for the lead phosphate-water-silica system was calculated as 1.7×10^{-20} J using Equation B.11 (Appendix B). The DLVO model (Equations B.9 and B.10, Appendix B) was then applied to compute interaction energy profiles at various IS, and the CDC was estimated to be ≈ 100 to 150 mM IS (**Figure B.8**) if it is assumed that the repulsive energy barrier must be fully diminished to zero for fast deposition. However, again a secondary energy minimum was observed in the DLVO profiles. Tufenkji and Elimelech previously discussed the importance of this secondary energy minimum in column deposition experiments with latex particles and the possibility for dual modes of deposition: one in the secondary energy well and a second by overcoming the primary energy barrier.¹¹⁸ For their particles, a secondary energy minimum with depth ($\Phi_{2\min}$) of $3.6 k_B T$ was computed at 10 mM IS, and estimated to result in $\alpha_{2\min}$ of 0.93 for deposition in the secondary minimum using Maxwell model proposed by Hahn and O'Melia. The attachment efficiency for deposition in the secondary minimum ($\alpha_{2\min}$) is defined as the probability that a particle cannot overcome the effective barrier of the secondary minimum to escape, which is expressed as

$$\alpha_{2\min} = 1 - \int_{E_{act}}^{\infty} f_{Max}(v_p) dv_p, \quad (3.1)$$

where E_{act} is the activation energy of the reaction which equals to $\Phi_{2\min}$ here, $f_{Max}(v_p)$ is the Maxwell distribution, v_p is the particle velocity.¹¹⁹ This expression requires numerical integration. In contrast, an exceedingly large primary energy barrier of nearly $5000 k_B T$ was computed as the repulsive barrier to primary deposition at 3 mM IS. Hahn and O'Melia note that secondary deposition is expected to become more important than primary deposition when the height of the primary energy barrier

exceeds $10 k_B T$.¹¹⁹ For the lead phosphate particles here, the primary energy barrier is not predicted to be eliminated until the IS reaches between 100 and 150 mM. However, a secondary energy minimum of $3.8 k_B T$ develops at 50 mM at particle-sand separation distance of ≈ 7 nm, with a primary energy barrier of $90 k_B T$, suggesting that rapid deposition in the secondary minimum can be dominant.

To compare the observed experimental results to the DLVO predictions, the experimental attachment efficiency α must be estimated at each condition, typically by applying colloid filtration theory as in Equation B.12 (Appendix B) with the single collector efficiency η_0 estimated from the particle, substrate, and flow conditions using Equation B.13 (Appendix B). As noted, the final C/C_0 measured after 10 PV in the deposition experiments are clearly impacted by ripening. However, we hypothesized that the plateau extrapolated from the initial portion of the breakthrough curve for the freshly prepared suspensions (where ripening may not yet have been initiated) might be predicted by DLVO theory, and hence used the extrapolated C/C_0 to parameterize Equation B.12 (Appendix B) to calculate experimental α values. The attachment efficiency versus IS was then plotted to extrapolate an experimental CDC value (note only a limited number of data from 10 mM to 15 mM IS were available where breakthrough could be extrapolated). Following this procedure, the experimental CDC was estimated to be ≈ 20 to 30 mM (**Figure B.9**), which is likely still influenced by the occurrence of ripening and hence somewhat underestimated. However, this CDC is on the order of magnitude of IS where a secondary minimum is observed in the DLVO interaction energy profile, but well below the CDC for primary deposition. Hence, lead phosphate particle transport in the absence of ripening and

straining may be predictable using DLVO theory, but only if deposition in the secondary minimum is considered. At high particle concentrations as evaluated here, ripening and straining must also be considered. In summary, considering the primary energy barrier from DLVO modeling largely overestimates the CDC.

3.3.2 Influence of P/Pb Ratio, Divalent Cations, and Humic Acid on Lead Phosphate Aggregation and Deposition

3.3.2.1 Precipitation and Aggregation of Lead Phosphate in Varied Water Chemistries

Further experiments were conducted when reducing the P/Pb ratio to $R_{P/Pb} = 1$ (Set II in **Table 3.1**), introducing divalent cations as Ca^{2+} at 0.2 mM or 1 mM (Set III), and introducing HA at 0.05 mg C/L or 5 mg C/L with 0.2 mM Ca^{2+} (Set IV). For all conditions except in the presence of 5 mg C/L, the particle size grew to over 1000 nm within 15 min, whereas the presence of HA at 5 mg C/L stabilized the particles (229 ± 25 nm) even after 21 h in 0.2 mM Ca^{2+} (**Figure 3.2a**).

For Sets II and III, the degree of aggregation corresponded well to loss of electrostatic stabilization as evaluated through the zeta potential measurements. At low P/Pb ratios, the particles exhibit a weak positive charge (3.1 ± 0.2 mV), likely due to reduced phosphate adsorption (**Figure 3.2c**). The weak charge is consistent with the rapid aggregation. However, the proportion of dissolved (< 0.1 μ m) lead was also notably higher with lower phosphate addition (6.22 ± 0.01 mg/L for $R_{P/Pb} = 1$ compared to 0.7 ± 0.1 mg/L for $R_{P/Pb} = 10$).

In the presence of 0.2 and 1 mM Ca^{2+} , particles were less negatively charged (-25.9 ± 0.8 and -15.1 ± 0.5 mV) than in the absence of Ca^{2+} (-42.1 ± 0.4 mV) due to

charge neutralization or screening. It was also considered that Ca substitution could occur during the particle precipitation: based on GWB calculations (**Table B.2**, set III), all initial solutions (**Table 3.1**, set III) were supersaturated with hydroxylpyromorphite ($SI = 21.2 \pm 0.1$), hydroxyapatite ($SI = 6.8 \pm 2.4$), $Pb_3(PO_4)_2$ ($SI = 12.6 \pm 0.1$), $PbHPO_4$ ($SI = 3.5 \pm 0.0$), $Pb_3(CO_3)_2(OH)_2$ ($SI = 4.6 \pm 0.0$), $Pb(OH)_2$ ($SI = 1.5 \pm 0.0$), and $PbCO_3$ ($SI = 1.3 \pm 0.0$). However, from Raman measurements in our previous work, no Ca substitution was observed.¹⁰⁰

For Set IV including HA, particle stability could not be explained solely by electrostatic effects. In the presence of 0.2 mM Ca^{2+} and 0.05 mg C/L of HA, the particles were indeed less negatively charged (-26.5 ± 0.8 mV) and showed more extensive aggregation than without Ca^{2+} or HA. However, the stabilizing influence of the higher concentration (5 mg C/L) of HA could not be explained by electrostatic effects, as the zeta potential (-33.4 ± 1.4 mV) was less negative than in monovalent electrolyte solutions where aggregation was observed (**Figure 3.2**). Hence, the stabilization by high HA concentrations is attributed to steric repulsion from the adsorbed HA. To investigate the effect of the observed particle aggregation or stabilization, the aged suspensions were evaluated further in column deposition experiments.

3.3.2.2 Lower $R_{P/Pb}$ and Higher Ca^{2+} Promote Deposition and Straining

Under high $R_{P/Pb} = 10$ without Ca^{2+} , a relatively high recovery rate of total lead was obtained. When $R_{P/Pb}$ was decreased to 1 or when increasing concentrations of Ca^{2+} were present in the background solution, much lower total lead was detected in

effluents (**Figure 3.4a**). Notably, slow breakthrough of lead from the $< 0.1 \mu\text{m}$ fraction appears for $R_{\text{P/Pb}} = 1$ (**Figure B.10a**), corresponding to the higher dissolved lead concentration measured in the original precipitated sample. This dissolved portion of lead exhibits reversible sorption to the sand (i.e., high retardation) with minimal irreversible attachment (i.e., the plateau concentration is similar to that in the injected suspension).

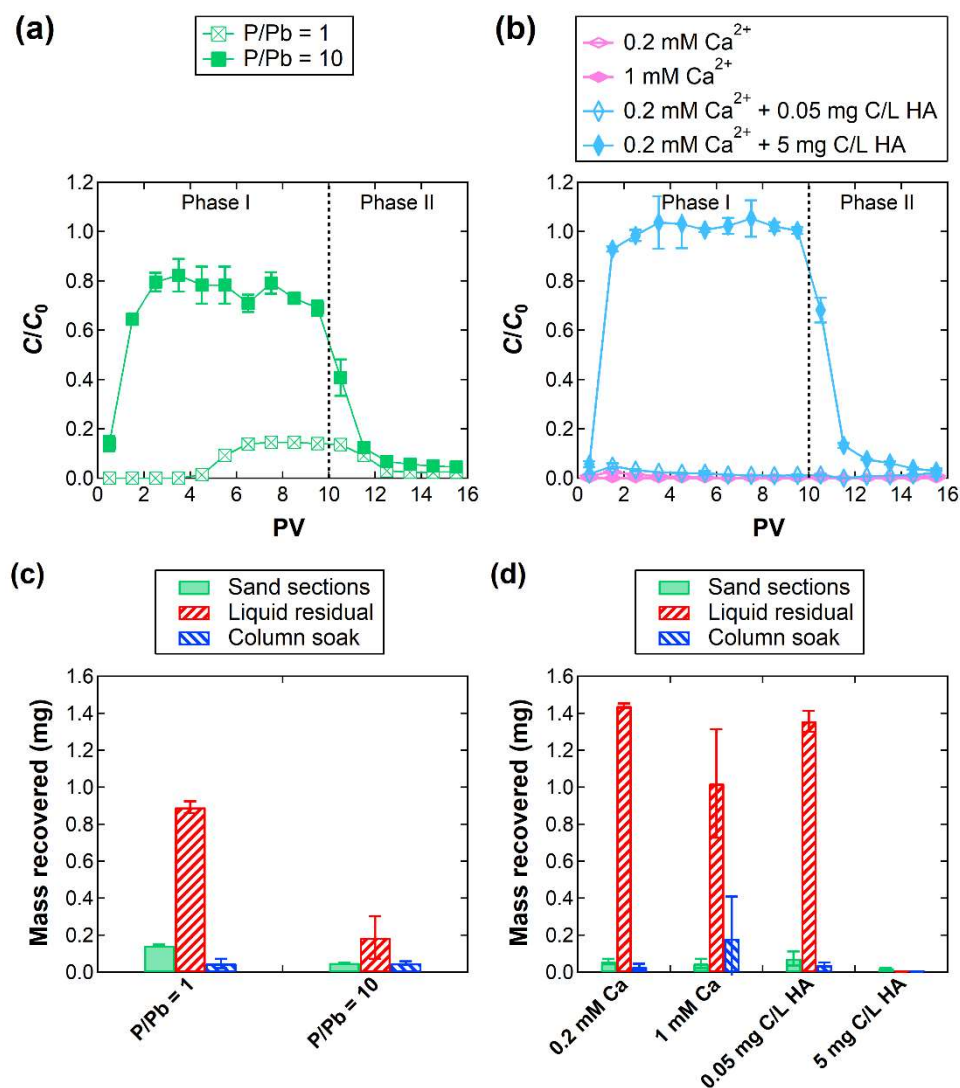


Figure 3.4. Breakthrough curves of total lead under $R_{\text{P/Pb}} = 1$ and 10 (a) or in the presence of Ca^{2+} with or without varying concentrations of HA (b), and lead mass recovered at the end of the corresponding experiments (c, d).

For $R_{P/Pb} = 1$ and 0.2 mM or 2 mM of Ca^{2+} , the mass recovery of lead from the column again shows the vast majority of the lead is present in the liquid residual, rather than the sectioned sand (**Figure 3.4c,d**). Given these results and the large aggregates formed under these conditions (**Figure 3.2**), the high removal in the column is likely primarily attributable to straining or perhaps attachment in a shallow secondary minimum, rather than strong attachment to the sand substrate.

3.3.2.3 Presence of Moderately High Concentration of Dissolved Humic Acid Inhibits Deposition

Deposition studies were finally performed with varying concentrations of HA under a condition where extensive particle removal was observed (0.2 mM Ca^{2+}). The low concentration of HA (0.05 mg C/L) did not effectively counter the extensive aggregation or deposition observed in the presence of Ca^{2+} without HA (**Figure 3.4b**) and most of the mass of lead in the column was recovered in the liquid residual (**Figure 3.4d**). However, the presence of 5 mg C/L of HA results in a remarkably high recovery rate of total lead was ($C/C_0 \approx 1.0$ in the column effluent) (**Figure 3.4b**), and correspondingly, lead retention in the column was extremely low in presence of 5 mg C/L of humic acid (**Figure 3.4d** and **Figure B.11b**). NOM is commonly reported to show inhibitory effects on attachment due to both electrostatic and steric repulsion.¹⁰⁰ However, the zeta potentials of the sand colloids and lead phosphate particles were similar or even less negatively charged in the combined presence of 0.2 mM Ca^{2+} and 5 mg C/L of HA than under other conditions in $NaNO_3$ where extensive deposition had been observed. Therefore, electrostatic repulsion cannot be the controlling

mechanism for the enhanced stability. Instead, the enhanced transport is attributed to steric repulsion caused by the HA, consistent with previous studies.¹²⁰

Given that the presence of HA can apparently inhibit all forms of deposition observed under other conditions (particle-substrate attachment, ripening, and straining of aggregates), the strong stabilizing effect of the HA as well as the HA concentration must be considered to predict lead phosphate transport in soils. Predicting these effects will be challenging as information on the HA layer thickness and layer density or adsorbed mass on the particles will be required in extended DLVO theories that include steric forces.

3.4 Conclusions

This research identified that lead phosphate transport can ultimately be challenging to predict across a range of potential soil porewater chemistries. First, several mechanisms of particle removal were identified to be important even in simple monovalent electrolyte, including (1) deposition in secondary minima, (2) ripening to previously deposited particles, and (3) straining of large aggregates. The ripening and straining phenomena can be particularly difficult to predict, as the influence of particle-particle interactions was exaggerated in the deposition studies compared to homoaggregation studies. The presence of low levels of Ca^{2+} can induce rapid aggregation and straining. On the other hand, when HA is introduced, all forms of particle removal can be negated by steric repulsion given a sufficiently high HA concentration. Hence, characterization of the ionic strength, electrolyte composition, and HA concentration will all be important to predict lead phosphate transport.

This study also identified that the implementation of the phosphate remediation strategy can be tuned to optimize lead removal. Notably, excessive application of phosphate can result in electrostatic stabilization by adsorbed phosphate and enhanced transport. However, lower phosphate concentrations are less effective to precipitate the lead phosphate. Hence, an intermediate phosphate concentration would be favorable to minimize total lead transport. However, given the potentially predominant influence of water chemistry on the results, further testing will be required that can potentially inform guidance on soil conditions where phosphate remediation can be effective to immobilize lead. For example, the results of this study can inform the design of response surface methodology studies to explore a wider combination of parameters. Finally, bench-scale and pilot-scale tests are necessary to verify the deposition behaviors of lead phosphate particles in real-world situations.

CHAPTER 4. EFFECTS OF NOM ON AGGREGATION OF LEAD PHOSPHATE PARTICLES

4.1 Introduction

Lead contamination is common due to exposure to various lead sources. As a result, elevated blood lead levels have been reported worldwide.^{121–123} High lead concentrations in blood threaten health of human, especially that of children. To be specific, excess of lead can arouse severe problems in multiple systems including nervous, skeletal, and immune systems.¹²⁴

Phosphate addition is regarded as an effective method to immobilize lead due to formation of lead phosphate with low solubility.⁹⁹ In environmental engineering, phosphate species such as apatite have been widely used to immobilize Pb in lead contaminated sites.^{125–127} Mavropoulos et al. conducted batch experiments to test sorption of Pb by synthetic HAP. They found an unstable solid solution, $\text{Pb}_{(10-x)}\text{Ca}_x(\text{PO}_4)_6(\text{OH})_2$ (PbCaHAP), formed, and eventually it transformed to pure hydroxylpyromorphite ($\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$, HPY).¹²⁵ However, stability of lead phosphate particles can be impacted by several environmental variables, thus controlling the treatment efficiency.

Natural organic matter (NOM), which is commonly presented in both aquatic environments and soils, can affect the aggregation behaviors of nanoparticles. Previous studies have reported that aromaticity and molecular weight can impact the stability of nanoparticles,^{6,128–130} while multiple functional groups including carboxyl, amine, and thiol groups can bind to lead ion or particle surfaces.^{131–133} For instance,

Deonarine et al. observed that aggregation rate of ZnS nanoparticles decreased with increasing aromatic carbon content in NOM.¹²⁹ Yin et al. found that higher molecular weight (MW) NOM fractions promoted the aggregation of PVP coated Ag nanoparticles in mono- and divalent electrolyte solutions, whereas lower MW NOM fractions showed inhibitory effect on particle aggregation.¹³⁰

To date, a few studies have been carried out to understand effect of small organic acids or in whole soil for lead immobilization. Li et al. compared reduction of Pb availability in three types of soils with different pH treated with bioapatite in the presence and absence of oxalic acid, and claimed that oxalic acid facilitated the remediation as it increased the solubility of apatite and that the soil with neutral pH was the most suitable type for this remediation.¹²⁷ Wei et al. also reported the similar observation for oxalic acid. In addition, they stated that the presence of malic and citric acids inhibited the immobilization of Pb by apatite materials due to the formation of Pb-organic complex.¹³⁴ Landrot and Khaokaew fractionated soil by size and measured speciation of Pb in each fraction. They found that Pb-humate in fine particles was the highest, while it was undetected in bulk soil, which may affect the efficiency of lead immobilization.¹³⁵ To our knowledge, a study of intermediate complexity between low molecular weight organic acids and whole studies is lacking. Therefore, a mechanistic understanding of the effect of more realistic NOM species on the aggregation of lead phosphate particles is still not well understood. Hence, a study that systematically evaluates the effect of well-characterized NOM that are extracted from realistic sources would be useful to delve more deeply into the interactions between NOM and lead phosphate particles.

The main goal of this study is to utilize well-characterized reference NOM extracts to identify properties of macromolecular NOM that control particle size and aggregate structure of lead phosphate particles. To fulfill this goal, aggregation experiments of lead phosphate particles were carried out in presence and absence of NOM and Ca^{2+} . Size and zeta potential of particles were measured using dynamic light scattering (DLS). Single particle ICP-MS (spICP-MS) and static light scattering (SLS) were employed to characterize structure of aggregates. Size exclusion chromatography (SEC) was coupled with ICP-MS to measure Pb-NOM complexation. It can help consolidate the understanding of how organics impact the aggregation of lead phosphate particles, and help strengthen the performance of lead remediation using phosphate.

4.2 Materials and Methods

4.2.1 Precipitation of Lead Phosphate Suspensions

Stock solutions of 10 mM $\text{Pb}(\text{NO}_3)_2$ (ACS reagent, $\geq 99.0\%$, Sigma-Aldrich, St. Louis, MO), 100 mM Na_2HPO_4 (99+ %, Acros Organics, Morris Plains, NJ), 100 mM NaH_2PO_4 (99%, Acros Organics, Morris Plains, NJ), and 1 M NaNO_3 (ACS reagent, $\geq 99.0\%$, Sigma-Aldrich, St Louis, MO) were prepared using aerated ultrapure water (resistivity $> 18 \text{ m}\Omega$). Then stock solutions were mixed to produce lead phosphate particles (**Table 4.1**). According to DLS measurements, size of lead phosphate particles formed were $228 \pm 4 \text{ nm}$. The zeta potential was $-39.6 \pm 0.1 \text{ mV}$. The concentration of lead phosphate particles in the precipitation solution was $20.5 \pm 0.7 \text{ mg/L}$.

Table 4.1. Experimental condition for formation of lead phosphate particles

Pb, mM	P, mM	NO ₃ ⁻ , mM	Na ⁺ , mM	IS, mM	pH ^a	SI ^b
0.10	1.00	3.20	4.49	5	7.0	21.1

Note: pH^a was calculated using GWB based on initial solution conditions. pH was measured at the beginning and end of the DLS measurements, and no significant differences were observed. SI^b: saturation index of hydroxylpyromorphite.

4.2.2 Preparation and Characterization of NOM Stocks

Four types of NOM were selected with different properties, where we expect we might observe distinct aggregation behaviors in presence of these NOM: Leonardite and Pahokee Peat humic acid (cat. no. 1S104H, and cat. no. 1S103H, International Humic Substances Society, St. Paul, MN), and Suwannee River and Upper Mississippi River NOM (cat. no. 2R101N, and cat. no. 1R110N, International Humic Substances Society, St. Paul, MN). **Tables 4.2** and **4.3** show the properties of the selected NOM, including their elemental compositions and functional group distributions.¹³⁶ According to the different isolation methods used to extract these NOM from raw materials, Suwannee River and Upper Mississippi River NOM, as aquagenic NOM, contain more hydrophilic contents, whereas pedogenic NOM like Pahokee Peat HA contain more hydrophobic components and have higher molecular weight,¹³⁷ which was confirmed by Louie et al. by utilizing size exclusion chromatography with multiangle light scattering (SEC-MALS).¹²⁸ From **Tables 4.2** and **4.3**, carboxyl density increases following the sequence of Leonardite HA (LHA), Pahokee Peat HA (PPHA), Suwannee River NOM (SRNOM), and Upper Mississippi River NOM (UMRNOM), while aromaticity increases following the opposite

sequence. For S content, it shows that Upper Mississippi River NOM > Suwannee River NOM > Leonardite HA > Pahokee Peat HA, and it shows Pahokee Peat HA > Upper Mississippi River NOM > Suwannee River NOM > Leonardite HA for N content. In summary, the variation of their properties may enable us to figure out how parameters like molecular weight and functional groups affect aggregation of lead phosphate particles.

Table 4.2. Elemental composition and functional group distributions of selected NOM¹³⁶

NOM type	Elemental composition ^a						Total concentration of amino acids ^b	Total concentration of carbohydrate ^c	Acidic functional groups ^d	
	C	H	O	N	S	P			Carboxyl	Phenolic
Leonardite HA	63.81	3.70	31.27	1.23	0.76	<0.01	11	2.6	7.46	2.31
Pahokee Peat HA	56.37	3.82	37.34	3.69	0.71	0.03	373	100	9.01	1.91
Suwannee River NOM	50.70	3.97	41.48	1.27	1.78	nd	nd	nd	11.21	2.47
Upper Mississippi River NOM	49.98	4.61	41.4	2.36	2.62	nd	nd	nd	12.43	0.83

Note: a: elemental composition in %(w/w) of a dry, ash-free sample; b,c: units are $\mu\text{mol/g}$; d: carboxyl is the charge density (meq/g C) at pH 8.0, phenolic is two times the change in charge density (meq/g C) between pH 8.0 and pH 10.0. nd means not determined.

Table 4.3. ¹³C NMR estimates of carbon distribution of selected NOM^{a136}

NOM type	Carbonyl	Carboxyl	Aromatic	Acetal	Heteroaliphatic	Aliphatic
	220-190 ppm	190-165 ppm	165-110 ppm	110-90 ppm	90-60 ppm	60-0 ppm
Leonardite HA	8	15	58	4	1	14
Pahokee Peat HA	5	20	47	4	5	19
Suwannee River NOM	8	20	23	7	15	27
Upper Mississippi River NOM	3	14	19	7	20	37

Note: a: percentages calculated from peak areas of ¹³C NMR spectra.

Stock solutions of the four types of organic matter were prepared. Glass vials were cleaned, heated in oven at 550°C for 2 h, and cooled at room temperature. For each type, 20 mg of NOM was dissolved in a clean glass vial filled with 20 mL ultrapure water. pH of the NOM solution was adjusted to 7 using 0.1 and 1 M NaOH. Then the vial with the NOM solution was rotated end-over-end overnight. After rotation, the solutions were filtered through 0.22 μm polyethersulfone (PES) membrane filters (EMD Millipore, Burlington, MA), and the filtrate was measured using TOC analyzer (TOC-L, Shimadzu) to obtain C concentration.

To determine molecular weight, the filtered NOM stocks (1 g/L) were characterized by size exclusion chromatography (SEC). All the samples were injected using a 100 μL injection volume into a Superdex 75 10/300 GL analytical SEC column (GE Healthcare, Piscataway, NJ) on an Agilent 1290 Infinity liquid chromatography system (Agilent Technologies, Santa Clara, CA), followed by UV (Agilent), multi-angle light scattering (MALS, HELEOS II, Wyatt Technology, Santa Barbara, CA), and differential refractive index (dRI) (Wyatt Technology) detectors. The mobile phase was 4 mM phosphate (pH 7) with 25 mM NaCl and flow rate was 0.5 mL/min. The UV detector was set to monitor the 280 nm wavelength. Molecular weight was estimated on the NOM samples using the dRI detector for concentration and Zimm plot analysis on the MALS data. The refractive index increment, dn/dc , is required to determine mass concentration from the dRI signal. Measured values of 0.146 mL/g for SRNOM¹³⁸ and 0.27 mL/g for PPHA¹²⁸ were obtained from prior studies. The dn/dc was not measured on the other two types of NOM, but for comparison purposes, the dn/dc of 0.146 mL/g was used for UMRNOM (which is expected to be more similar to the SRNOM) and 0.27 mL/g for LHA (which is expected to be more

similar to the PPHA). Samples were prepared by Juntao Zhao, and Stacey Louie conducted the SEC measurements.

4.2.3 Aggregation Experiments

To characterize aggregation behaviors of lead phosphate particles in presence of NOM, dynamic light scattering (DLS) measurements were conducted. Stock solution of 10 mM $\text{Ca}(\text{NO}_3)_2$ (from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, ACS reagent, 99+%, Acros Organics, Morris Plains, NJ) was prepared using aerated ultrapure water (resistivity $> 18 \text{ m}\Omega$). NOM stock and lead phosphate suspension were mixed with ultrapure water in a cuvette cell (ZEN0040, Malvern Instruments Ltd.). The mixture was vortexed for 5 s and let sit for 15 min to allow NOM adsorption, and the particle size was measured every 3 min. Lastly, $\text{Ca}(\text{NO}_3)_2$ or NaNO_3 was added to the mixture to achieve a Ca^{2+} concentration of 1 or 3 mM or a Na^+ concentration of 100 mM. NOM concentration was 1 or 10 mg C/L, and concentration of lead phosphate particles was 1 mg/L in the final mixture. These NOM concentrations were selected because they are within the typical dissolved organic carbon (DOC) concentration range in natural waters (0.5-30 mg C/L).¹³⁷ The electrolyte concentrations were selected because they are all around or above CCC, which would allow us to identify most clearly the influence of the NOM to either stabilize particles, i.e., change the CCC, or destabilize the particles by bridging, i.e., more rapid agglomeration than the “diffusion” limit. The final mixture was vortexed for 5 s and then measured by DLS (Zetasizer, Malvern Instrument Ltd.). Particle size was recorded every 15 s for 15 min continuously. To make a comparison, similar measurements were conducted in the absence of any additional salts (Ca^{2+} or Na^+). All conditions were triplicated. At the end of the size measurement, a dip cell (ZEN1002, Malvern Instruments Ltd.) was capped on the cuvette

cell, and zeta potential was measured. To determine mechanisms of decrease in particle size in presence of 10 mg C/L NOM, aggregation experiments were also conducted without addition of lead phosphate particles. Lead phosphate particles as well as NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, and NOM stocks were prepared by Juntao Zhao. DLS measurements were performed by Juntao Zhao, Utiyenin Pemu, and Chinasa Nwachukwu.

4.2.4 Adsorption Experiments

4.2.4.1 UV-vis Spectroscopy

To investigate adsorption of NOM onto lead phosphate particles, adsorption experiments were performed in a laminar flow hood (Air Science, Fort Myers, FL). Similar to DLS measurements, NOM, $\text{Ca}(\text{NO}_3)_2$ or NaNO_3 , lead phosphate suspension, and ultrapure water were mixed in a 2 mL microcentrifuge tube (Neptune Scientific) to get an organic concentration of 10 mg C/L, Ca^{2+} concentration of 1 or 3 mM or Na^+ concentration of 100 mM, lead phosphate particle concentration of 0 or 10 mg/L (which was to allow as much adsorption of NOM as possible to show any difference in absorbance, so the particle concentration was increased to 10 mg/L). The mixture was let sit for 15 min, and then centrifuged at 13000 rpm for 15 min. Then 1.8 mL of the supernatant was collected, 0.7 mL of which was measured by UV-Vis spectroscopy (UV-2600, Shimadzu, Columbia, MD). The spectra were collected using with a wavelength range from 800 to 200 nm and a sampling interval of 1.0 nm. For comparison, samples in the absence of lead phosphate particles without centrifuging were also measured. Samples with no addition of extra salts were prepared following the same procedure.

4.2.4.2 Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR measurements were conducted to characterize the functional groups of NOM adsorbed onto lead phosphate particles. NOM, lead phosphate suspension, and ultrapure water were mixed in a total volume of 12 mL to get an organic concentration of 10 mg C/L and lead phosphate particle concentration of 1 mg/L. The mixture was rotated for 15 min to keep consistent with the aggregation experiments, and then centrifuged using a pre-rinsed 100 kDa centrifugal filter (Millipore Sigma, Burlington, MA) at 5000 rpm for 5 min. Then the concentrated particles were washed once using ultrapure water to remove excess NOM. 6 μ L of the concentrated particles were deposited and dried on a diamond/ZnSe single reflection ATR crystal (PIKE Technologies, Fitchburg, WI), and FTIR spectra were collected on a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA) from 800 to 4000 cm^{-1} at 2 cm^{-1} resolution. The spectrum for each sample was subtracted by the one of water vapor. Samples were prepared by Juntao Zhao and FTIR measurements were performed by Riya Mathew.

4.2.5 Static Light Scattering (SLS) Measurements

To evaluate the fractal dimension of the aggregates, SLS measurements were conducted. Six conditions were selected (particles + ultrapure water, particles + 100 mM NaNO_3 , particles + 1 mM $\text{Ca}(\text{NO}_3)_2$, particles + 3 mM $\text{Ca}(\text{NO}_3)_2$, particles + 10 mg C/L PPHA + 3 mM $\text{Ca}(\text{NO}_3)_2$, and particles + 10 mg C/L LHA + 3 mM $\text{Ca}(\text{NO}_3)_2$), and samples were prepared following the same procedure as the aggregation experiments in a laminar flow hood (Air Science, Fort Myers, FL) and sat for 2 h before measurements.

To distinguish the possible contribution of NOM, two controls were also measured (10 mg C/L PPHA + 3 mM Ca(NO₃)₂, and 10 mg C/L LHA + 3 mM Ca(NO₃)₂).

SLS data were collected on an ALV instrument (ALV-GmbH, Germany). 600 µL of buffer solution was injected to a cuvette cell (540.111-QS, Hellma, Germany). DLS data (correlation and count rate) were first recorded at scattering angle (θ) of 90°, then scattering intensities (I) were detected at a scattering angle range of 30 – 150° with an angular step of 5°. After measuring the buffer solution, the cuvette cell was filled with 600 µL of sample. Similarly, correlation and count rate were recorded at scattering angle of 90°, and scattering intensities were detected at a scattering angle range of 30 – 150° with an angular step of 5°. Then scattering intensities were detected in a reverse direction (from 150 to 30° with an angular step of 10°) to check if there were any changes in intensities during the measurements. After one day, the samples were measured again to confirm whether the fractal dimension changed. Samples were prepared by Juntao Zhao and SLS measurements were taken by Juntao Zhao and David Yang.

The scattering vectors (q) were calculated using

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right), \quad (4.1)$$

where, n is solvent index of refraction (1.33 for water), λ is the wavelength of the incident light (632.8 nm). Log I (the intensities of sample subtracted by the intensities of the corresponding buffer) was plotted versus log q , and the slope of the trendline was used to assess the fractal dimension of the particles.

4.2.6 SEM Measurements

Eight conditions were selected (particles + ultrapure water, particles + 1 mM $\text{Ca}(\text{NO}_3)_2$, particles + 3 mM $\text{Ca}(\text{NO}_3)_2$, particles + 10 mg C/L PPHA + 1 mM $\text{Ca}(\text{NO}_3)_2$, particles + 10 mg C/L LHA + 1 mM $\text{Ca}(\text{NO}_3)_2$, particles + 10 mg C/L PPHA + 3 mM $\text{Ca}(\text{NO}_3)_2$, particles + 10 mg C/L LHA + 3 mM $\text{Ca}(\text{NO}_3)_2$, and particles + 10 mg C/L SRNOM + 3 mM $\text{Ca}(\text{NO}_3)_2$) for SEM measurements, and samples were prepared following the same procedure as the aggregation experiments in a laminar flow hood (Air Science, Fort Myers, FL) and sat for 5 h before measurements in order to get large aggregates that were potentially able to be detected by SEM. Then 20 μL of the suspension was transferred to copper tape stuck to metal holder and pre-rinsed with ultrapure water, let sit for 5 min to allow deposition, wicked off extra fluid, and let dry completely. After that, 20 μL of ultrapure water was applied to rinse excess salts and NOM, and fluid was wicked off. Then samples were allowed to dry, sputter-coated with gold, and measured by SEM. Details of SEM measurements can be found in Appendix A. Samples were prepared by Juntao Zhao, and SEM measurements were performed by Charisma Lattao and Juntao Zhao.

4.3 Results and Discussion

4.3.1 Characterization of the NOM Isolates

From the TOC measurement results, the measured concentrations of the stock solutions of PPHA, LHA, SRNOM, and UMRNOM were 431.06, 392.57, 391.49, and 359.51 mg C/L, respectively. Accordingly, the carbon content of PPHA, LHA, SRNOM,

and UMRNOM were 43%, 39%, 39%, and 36%. All the wt % carbon was lower than what are reported by IHSS, which was possibly due to the filter loss prior to the TOC measurement as well as the incomplete oxidation of the NOM during the TOC measurement.

UV–vis absorbance spectra were collected as shown in **Figure 4.1a**. The UV absorbance has previously been reported to correlate to the percent aromaticity of NOM, with Abbt-Braun et al. and Chin et al. reporting correlation equations based on the specific UV absorbance at 254 nm and 280 nm, respectively.^{139,140} Applying these correlations and averaging the results provides an estimated aromaticity of 26 %, 28 %, 51 %, and 62 %, for UMRNOM, SRNOM, PPHA, and LHA, respectively.

Then the spectra were fitted by an exponential model to solve for slope coefficient (S).¹⁴¹

$$A_{\lambda} = A_{\lambda_0} \exp [-S(\lambda - \lambda_0)] \quad (4.2)$$

where A_{λ} is the absorbance at wavelength λ , A_{λ_0} is the absorbance at a reference wavelength λ_0 (450 nm here). The exponential fits were plotted in **Figure 4.1b**. The S obtained for UMRNOM and SRNOM were similar (0.0139 and 0.0135 nm⁻¹, respectively), which were smaller than that of PPHA and LHA (0.0091 and 0.0089 nm⁻¹, respectively), implying that PPHA and LHA have higher molecular weight.

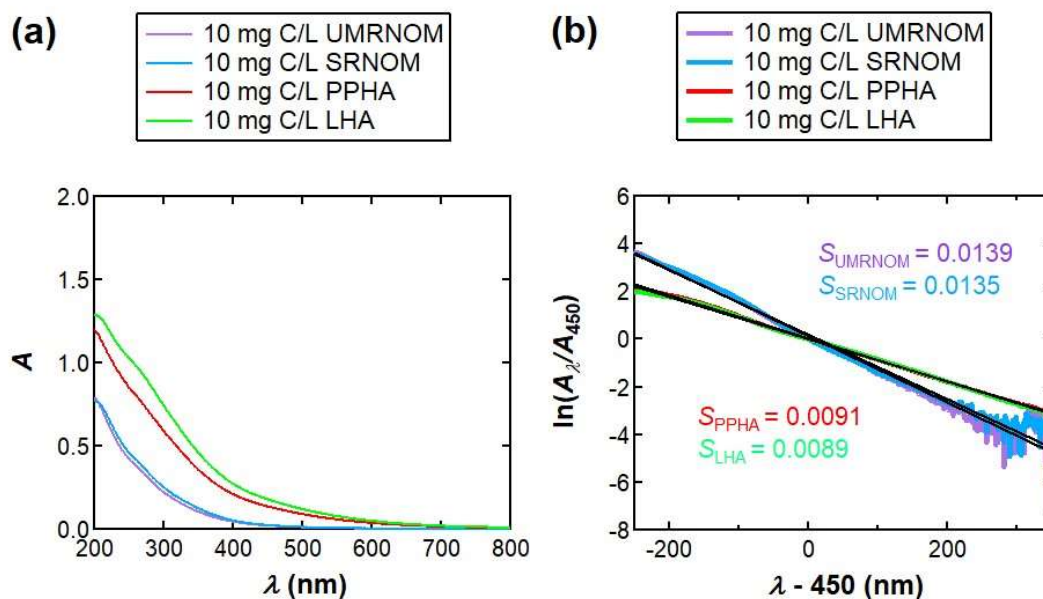


Figure 4.1. (a) UV-Vis absorbance spectra and (b) exponential fits for 10 mg C/L UMRNOM/SRNOM/PPHA/LHA.

The SEC results are shown in **Figure 4.2** for the molecular weight distribution. Note that the dRI results are influenced by dissolved gases or differences between the sample solvent and the SEC mobile phase; hence, molecular weight could only be determined across the initial portion of the chromatogram when using dRI as the concentration detector for the MALS analysis. The results for UMRNOM, SRNOM, and PPHA show good agreement with the UV spectral slope analysis: UMRNOM and SRNOM show very similar chromatograms with an estimated weight-average molecular weight of 31 kDa and 29 kDa, respectively, whereas PPHA shows a higher proportion of high molecular weight species with a weight-average molecular weight of 211 kDa. Note that the MALS analysis for PPHA also reveals adsorptive interactions (i.e., retardation) of the PPHA to the SEC column, with high molecular weight species eluting later than moderate molecular weight species. The LHA was visibly observed to adsorb strongly near the SEC

column inlet, with low recovery of LHA eluting out of the column. Therefore, the SEC-MALS analysis for LHA does not reliably represent its full molecular weight distribution, as the highest molecular weight species were lost in the column and could not be measured thereafter.

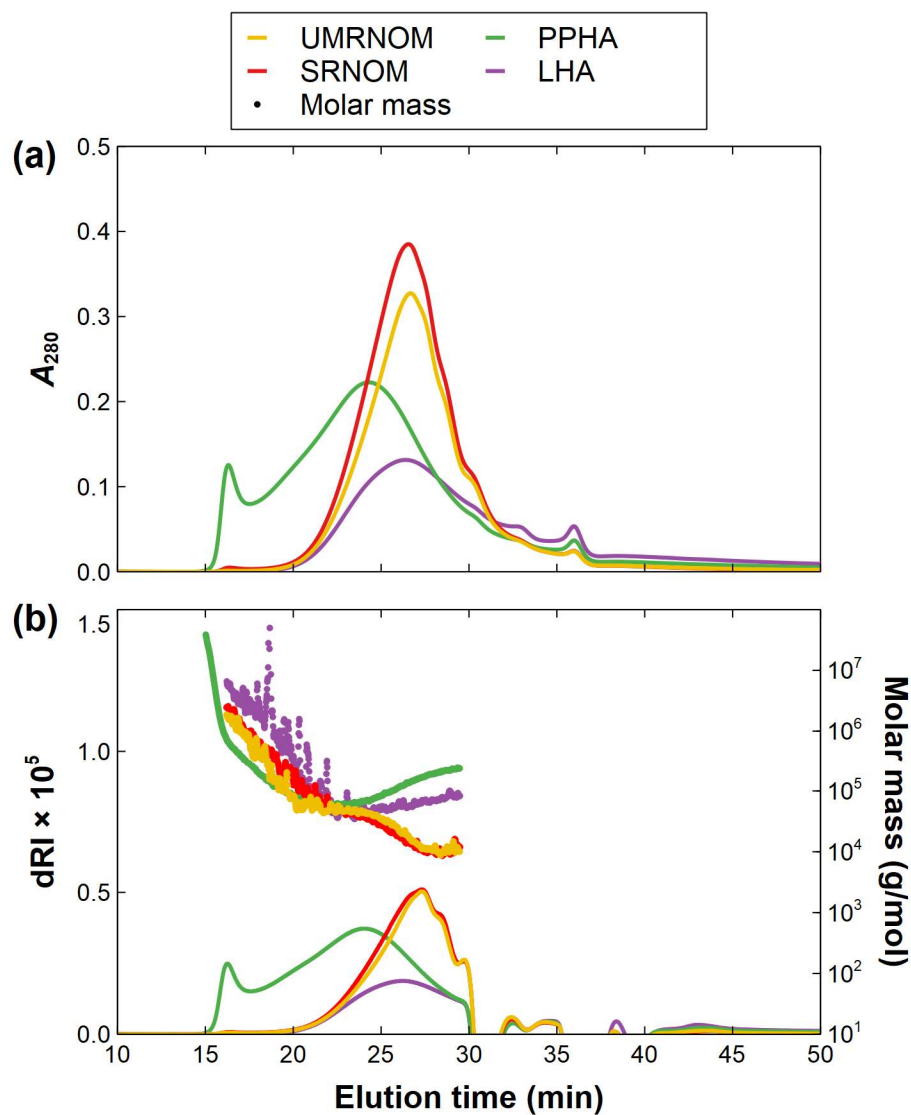


Figure 4.2. SEC chromatograms using (a) UV and (b) dRI detection, with SEC-dRI-MALS to determine molecular weight distributions on 1 g/L NOM samples. Note that LHA showed losses of high molecular weight species onto the SEC column.

4.3.2 Characterization of NOM Adsorption to Lead Phosphate Particles by ATR-FTIR Spectroscopy and UV-vis Spectroscopy

ATR-FTIR spectroscopy (**Figure 4.3**) was applied to evaluate NOM adsorption onto lead phosphate particles as recovered in the washed retentate of a 100 kDa centrifugal ultrafiltration device. The spectra of particles in presence of 10 mg C/L of SRNOM or UMRNOM was similar to that of particles just in ultrapure water, suggesting minimal adsorption. In contrast, the ATR-FTIR spectra of particles in the presence of 10 mg C/L of PPHA or LHA showed additional absorbances around 1600 cm^{-1} , which can be attributable to conjugated carbonyl and aromatic alkenes, or deprotonated carboxyl groups of adsorbed NOM.^{142–146} However, it is possible that these higher molecular weight NOM were not necessarily adsorbed to the particle surface but simply retained in the 100 kDa filter. Therefore, *in situ* ATR-FTIR experiments will be required to provide more definitive evidence of NOM adsorption. Furthermore, additional measurements should be collected across the range of water chemistries (i.e., with NaNO_3 or $\text{Ca}(\text{NO}_3)_2$) to further explore NOM adsorption that could influence the agglomeration behavior investigated hereafter.

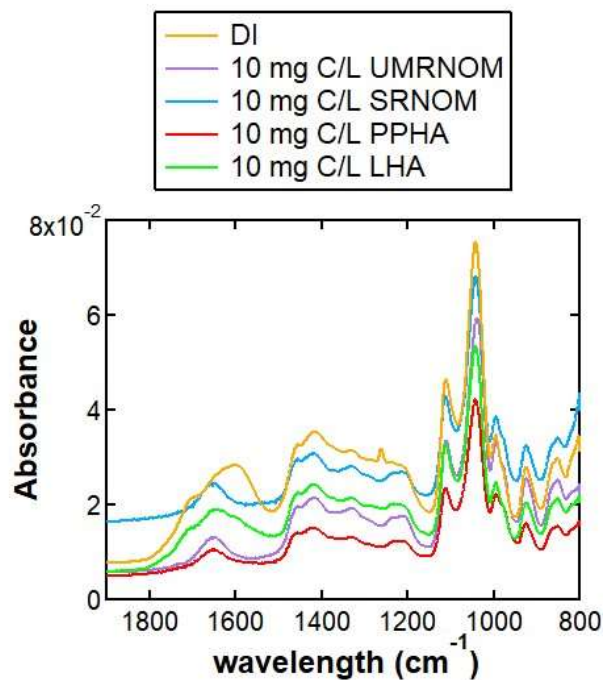
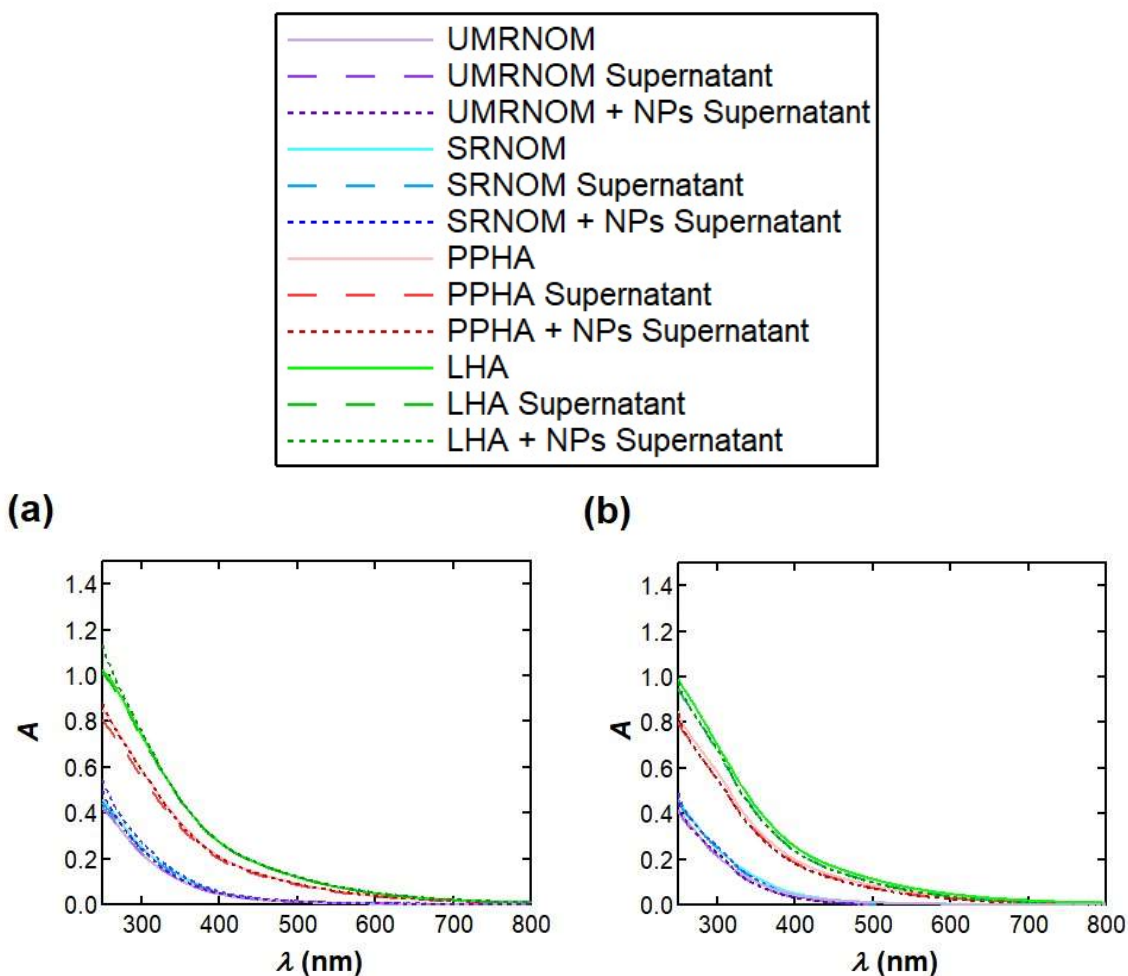


Figure 4.3. FTIR spectra of lead phosphate particles in ultrapure water, or in presence of 10 mg C/L UMRNOM/SRNOM/PPHA/LHA.

UV-Vis spectroscopy (**Figure 4.4**) was performed to compare the relative adsorption of NOM onto the Pb NPs by a solution depletion analysis, in which the remaining NOM in solution (i.e., in the supernatant after centrifugation) is compared to the total NOM added to evaluate loss by adsorption. Controls were also collected of the NOM in the various water chemistries without Pb NPs to account for any possible losses due to NOM self-aggregation. Note that the concentration of Pb NPs was increased to 10 mg/L to allow higher removal that can be more confidently measured. The influence of the absorbance of salts in the background were corrected by using the salt solution for baseline subtraction; particularly, NO_3^- produces a peak at 300 nm and shows strong absorbance at wavelengths lower than ≈ 250 nm. The data demonstrate accurate subtraction of the 300 nm peak (i.e., no peaks or valleys are observed at 300 nm after baseline subtraction), but the absorbance at < 250 nm resulted in transmittance below the limit of detection, and

hence only the data ≥ 250 nm are presented. In all the backgrounds, no measurable adsorptive losses to lead phosphate particles were observed for any of the NOM. However, absorbance drop was observed for PPHA and LHA supernatants in the presence of 3 mM Ca^{2+} (**Figure 4.4d**), indicating that the presence of high Ca^{2+} that induce bridging of the PPHA and LHA to form large, dense aggregates that settle after centrifuging. SEC measurements of all these samples might be needed to show evidence for distinguishable adsorption.



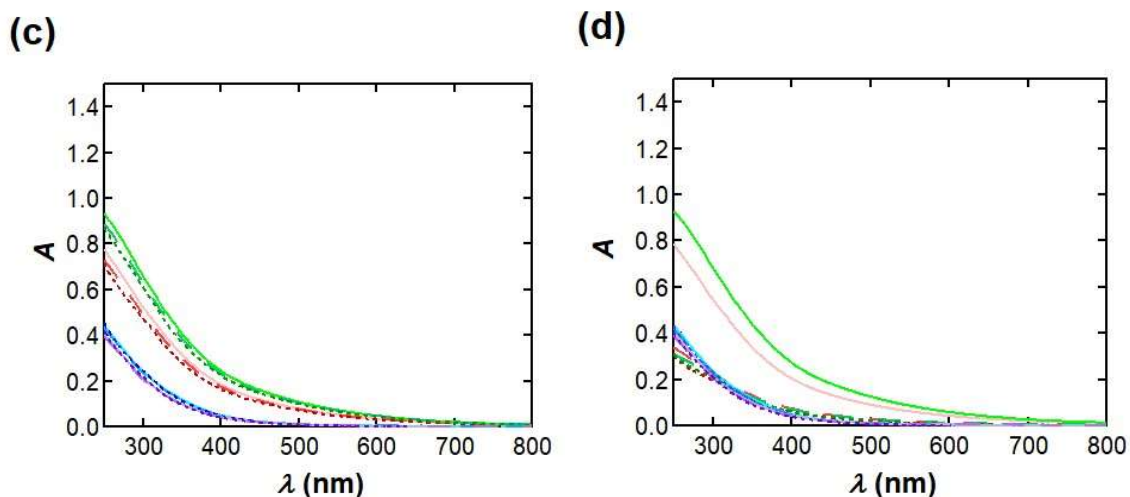


Figure 4.4. UV-vis spectra of 10 mg C/L NOM with or without 10 mg/L lead phosphate particles in (a) ultrapure water, or in presence of (b) 100 mM Na^+ , (c) 1 mM Ca^{2+} , (d) 3 mM Ca^{2+} .

4.3.3 Aggregation behavior of lead phosphate particles in the presence of different types and concentrations of NOM and different background electrolytes

Particles in the absence of any additional electrolytes were used as the control. Under these conditions, the particles showed no agglomeration regardless of the concentrations of NOM added (**Figure 4.5**). All particles were highly negatively charged (< -30 mV) according to the zeta potential measurements (**Figure 4.6**), which was consistent with electrostatic stabilization. Notably, particle sizes decreased in the presence of 10 mg C/L of the NOM (after 15 min, 198 ± 12 , 197 ± 16 , 166 ± 40 , and 143 ± 5 nm for UMRNOM, SRNOM, PPHA, and LHA, respectively), suggesting the NOM induced either disaggregation or dissolution of the particles. To further investigate the reason for the decreased particle sizes in the presence of higher concentration of NOM, aggregation experiments were conducted with 10 mg C/L NOM in different water chemistries. Results from SRNOM/UMRNOM were not included in the following figures as their sizes were

not measurable by DLS. From **Figure 4.5c**, PPHA and LHA were stable in ultrapure water, and their sizes were similar to the particle sizes shown in **Figure 4.5b**.

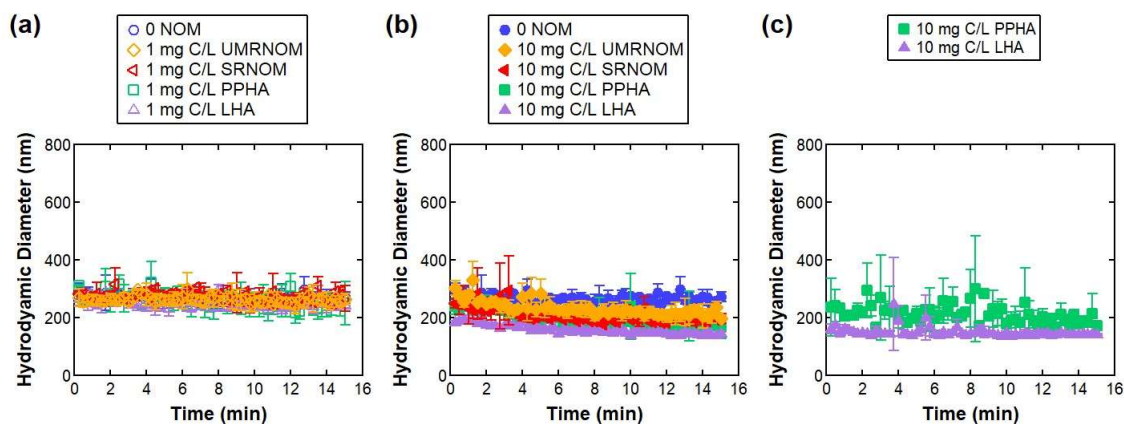
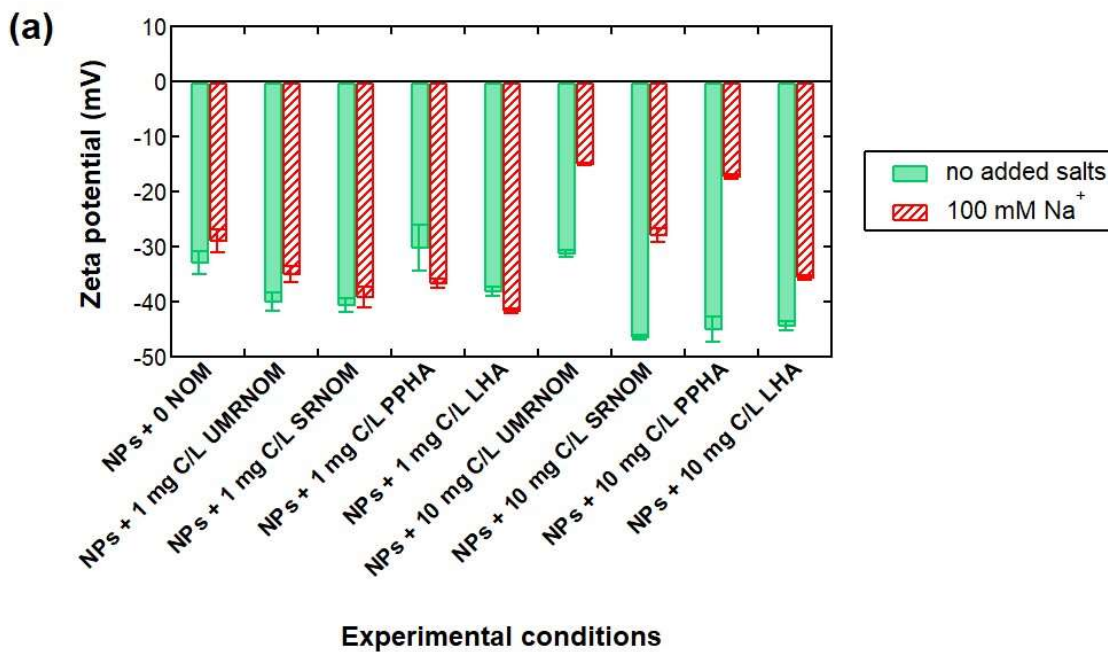


Figure 4.5. Size evolutions of lead phosphate particles in presence of (a) 1 mg C/L NOM, (b) 10 mg C/L NOM, and (c) size evolutions of 10 mg C/L PPHA/LHA in ultrapure water.



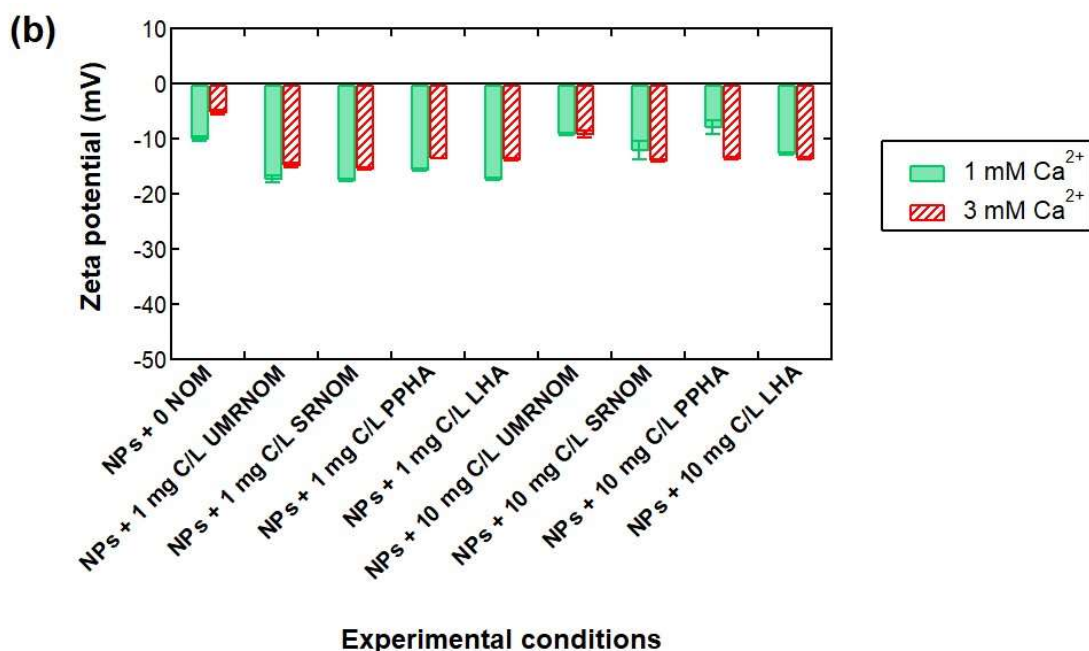


Figure 4.6. Apparent zeta potentials of lead phosphate particles (a) with no added salts or in presence of 100 mM Na^+ , (b) in presence of 1 or 3 mM Ca^{2+} .

In the presence of 100 mM Na^+ , lead phosphate particles were stabilized with either 1 or 10 mg C/L NOM (**Figure 4.7**). From Chapter 3, the CCC value for particles formed in water chemistries typical of soils was ~ 100 mM in monovalent electrolyte. Nevertheless, even such high IS was not able to induce agglomeration of the lead phosphate particles after they were pre-mixed with any of the four types of NOM. The electrophoretic light scattering measurements showed a less negative apparent zeta potential for 10 mg/L UMRNOM and PPHA compared to those in 100 mM Na^+ without NOM (**Figure 4.6**), despite the expectation that the carboxylate groups on the NOM should impart additional negative charge at pH higher than their pK_a as used here (pH 7). The possibility for high molecular weight NOM coatings to result in a less negative apparent zeta potential but impart colloidal stability was previously reported by Louie et al.,¹²⁸ and is likely

attributable to the fact that the electrophoretic mobility measured on the Zetasizer is influenced not only by charge but by the friction or drag on the particles.^{147–150} Thick or high molecular weight NOM coatings can induce more significant drag forces, therefore resulting in less negative electrophoretic mobilities. This effect is not considered in the Smoluchowski model used to convert electrophoretic mobility to zeta potential. Therefore, the zeta potentials reported here are merely apparent zeta potentials, rather than a true representation of amount of charge. Furthermore, as Romanello and Fidalgo de Cortalezzi discussed, compression of the electrical double layer may not be the controlling mechanism for aggregation in such situations.¹⁵¹ Rather, the NOM likely adsorbs to impart steric stabilization of the particles.

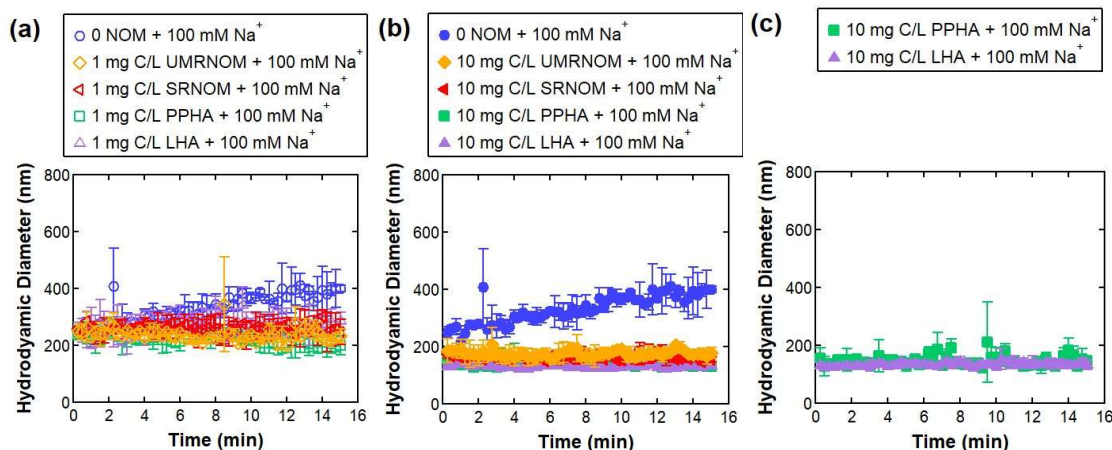


Figure 4.7. Size evolutions of lead phosphate particles pre-mixed with (a) 1 mg C/L NOM, (b) 10 mg C/L NOM, in presence of 100 mM Na⁺, and (c) size evolutions of 10 mg C/L PPHA/LHA in 100 mM Na⁺.

In the presence of 1 mM Ca²⁺, the particles were also stabilized after being mixed with 1 or 10 mg C/L NOM (**Figure 4.8**). However, particles pre-mixed with 10 mg C/L PPHA or LHA showed an even more drastic decrease in particle size than observed with no added electrolyte (**Figure 4.5**) or with 100 mM Na⁺ (**Figure 4.7**), i.e., the hydrodynamic

diameter was less than half that of the original particle sizes. According to the aggregation experiments of NOM, the PPHA and LHA sizes also decreased drastically in the presence of 1 mM Ca^{2+} (**Figure 4.8c**) compared to those in ultrapure water (**Figure 4.5c**), indicating intramolecular bridging occurred, leading to a collapse of the NOM structure. For the batch DLS data, it is not possible to distinguish whether the lead phosphate particles were disaggregated further by the NOM or whether the DLS size primarily reflects the NOM itself. However, it is clear that no aggregation is occurring, i.e., the PPHA and LHA are colloidally stable and further are stabilizing the particles relative to the case without NOM.

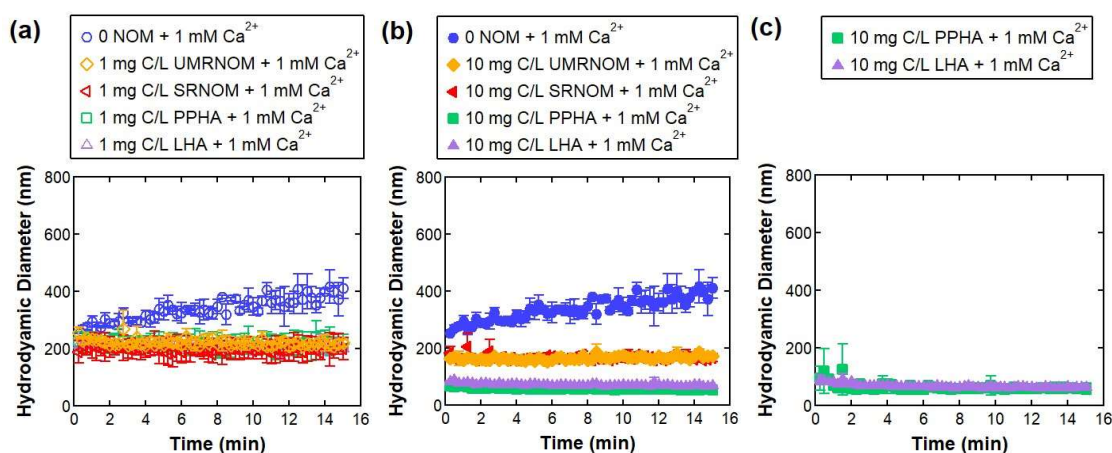


Figure 4.8. Size evolutions of lead phosphate particles pre-mixed with (a) 1 mg C/L NOM, (b) 10 mg C/L NOM, in presence of 1 mM Ca^{2+} , and (c) size evolutions of 10 mg C/L PPHA/LHA in 1 mM Ca^{2+} .

In the presence of 3 mM Ca^{2+} , the particles again remained stable when pre-mixed with lower concentrations (1 mg C/L) of any of the four types of NOM (**Figure 4.9a**), as well as with 10 mg C/L of the SRNOM or UMRNOM (**Figure 4.9b**). On the other hand, rapid aggregation occurred for particles pre-mixed with 10 mg C/L PPHA or LHA (**Figure 4.9b**). In fact, the aggregation rate (i.e., slope of hydrodynamic diameter versus time) was higher than that of the particles without NOM. As the Ca^{2+} concentration here is higher than the CCC for diffusion-limited aggregation of the bare particles, the faster rate of

aggregation is indicative that the destabilization by NOM is not purely electrostatic destabilization. Rather, enhanced aggregation rates have typically been attributed to a bridging phenomenon as proposed by Chen et al.¹⁵² Aggregation experiments of NOM showed that PPHA or LHA aggregated rapidly in presence of 3 mM Ca^{2+} (**Figure 4.9c**), which indicates that the HAs themselves can participate in intermolecular bridging given excess Ca^{2+} . Notably, the rate of size increase was also significantly higher for the lead NPs in the presence of the PPHA and LHA than the HA controls alone, indicating that the observed aggregation with the NPs is not simply an observation of HA aggregation. Rather, both the NPs and the HA participate in the aggregation process, resulting in large flocculates of particles with HA. SEM images of the aggregates are provided in Appendix C (**Figure C.1**).

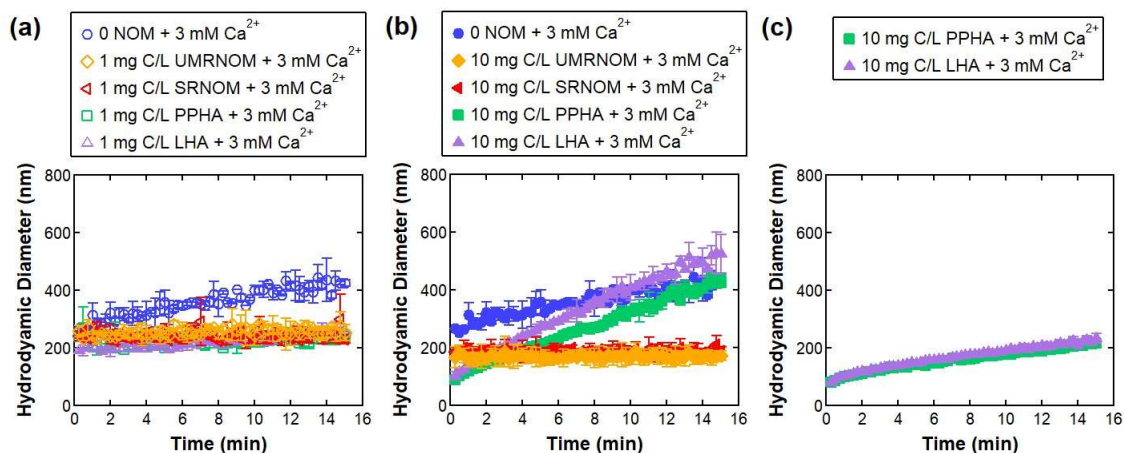


Figure 4.9. Size evolutions of lead phosphate particles pre-mixed with (a) 1 mg C/L NOM, (b) 10 mg C/L NOM, in presence of 3 mM Ca^{2+} , and (c) size evolutions of 10 mg C/L PPHA/LHA in 3 mM Ca^{2+} .

Figure 4.10 summarizes the aggregation results observed across all four types of NOM at the two concentrations (1 mg C/L or 10 mg C/L) in the four background water chemistries reported in **Figures 4.5, 4.7, 4.8, and 4.9**. Overall, the results show that the

NOM imparts colloidal stabilization under all conditions *except* when high molecular weight NOM (PPHA and LHA) are present at high concentrations (10 mg C/L) with high concentrations of Ca^{2+} (3 mM). These results overall are all consistent with a bridging phenomenon in which Ca^{2+} chelates to two separate carboxylate groups on the NOM to induce aggregation. The lead phosphate particles can then undergo more rapid agglomeration through either bridging of NOM coatings on the particles or by entrainment in NOM agglomerates. Romanello and Fidalgo de Cortalezzi's previously reported that bridging between Ca^{2+} and NOM required high Ca^{2+} concentrations,¹⁵¹ consistent with the finding here that 1 mM Ca^{2+} was not sufficient to initiate bridging. This study further identified that bridging only occurs for high molecular weight NOM when a sufficiently high concentration of the NOM is present.

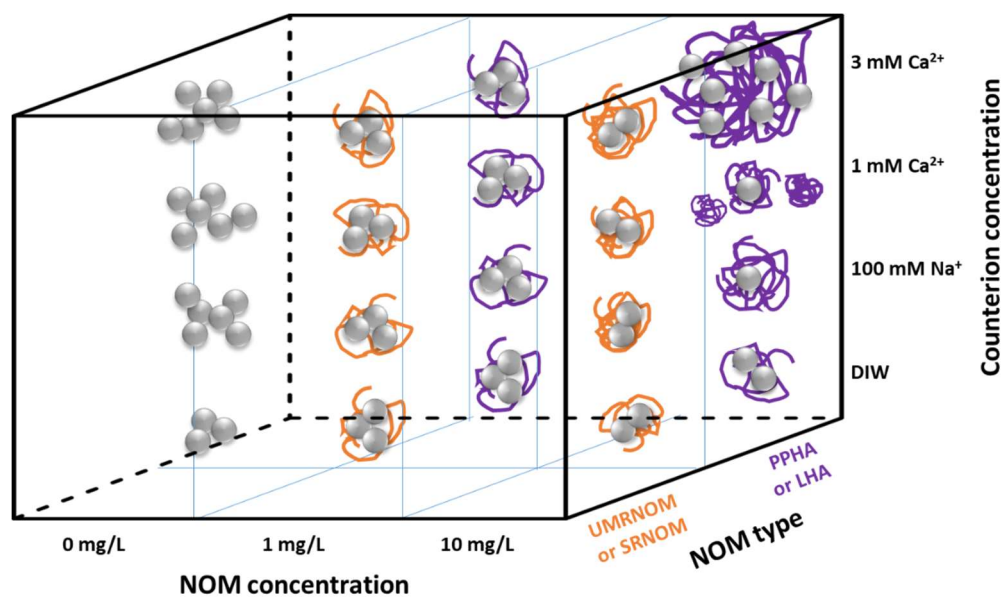


Figure 4.10. Summary of aggregation behavior observed depending on NOM concentration and type and the type and concentration of counterions.

4.3.4 Fractal Dimension Analysis by SLS

To further investigate the structure of the aggregated particles, SLS measurements were collected to compare the fractal dimensions of the aggregates of the bare particles in the various electrolytes and those with PPHA or LHA in 3 mM Ca^{2+} (**Figure 4.11**).

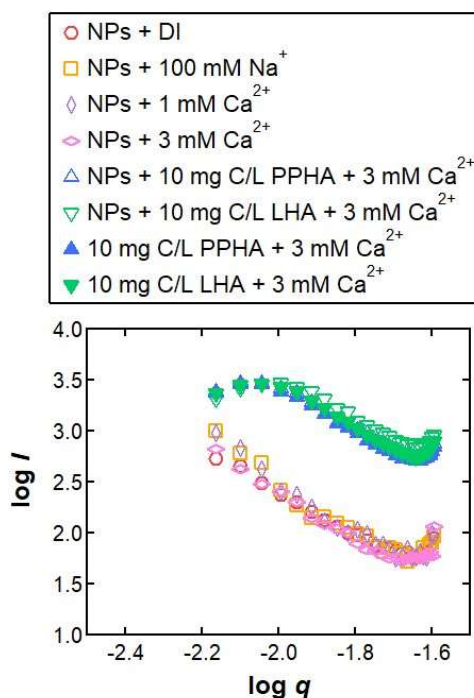


Figure 4.11. Log scattering intensities versus the log scattering vector for lead phosphate particles after 2 h.

In the fractal regime of scattering angles, the log-log plot of scattered light intensity ($\log I$) versus scattering vector ($\log q$) is linear, with the slope representing the fractal dimension of the aggregates.¹¹⁴ From **Figure 4.11**, the linear range for the samples without NOM appears to be scattering angles of $\leq 30^\circ$ to 105° (i.e., q of 0.007 to 0.021, or $\log q$ of -2.165 to -1.679), whereas the linear range for the samples with NOM appeared to be scattering angles of 45° to 120° (i.e., q of 0.010 to 0.023, or $\log q$ of -1.995 to -1.641). The reason for the difference in the linear ranges of the SLS plot for the particles without or

with NOM is not clear but may be attributable to different primary particle and aggregate sizes, which determine the range of wavelengths where the “fractal regime” applies. The slopes in the linear region for all the conditions tested are similar (**Figure 4.12**). Perhaps more notably, the overall intensity and shape of the SLS plots show that the PPHA and LHA themselves form highly scattering aggregates in the presence of 3 mM Ca^{2+} without any lead phosphate particles present. Some increase in intensity, but no significant difference in slope or fractal dimension is observed, when the lead phosphate particles are introduced. Therefore, the aggregate structure observed under these conditions by both DLS and SLS may be primarily attributable to the flocculated NOM, with lead phosphate particles more sparsely entrained throughout the NOM floc structure.

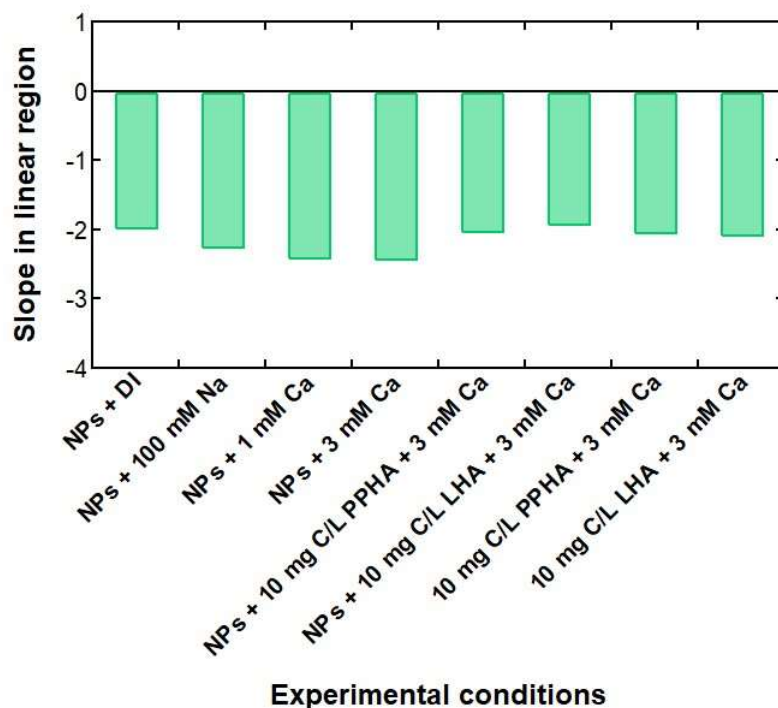


Figure 4.12. Slopes in linear region.

4.4 Conclusion

This research explores the range of influences of water chemistry – i.e., the composition and concentration of both NOM and background electrolytes – on the aggregation behavior of lead phosphate particles that can precipitate when phosphate is applied to remediate lead-contaminated environments. This study demonstrated that the specific water chemistry conditions will be critical to the transport behavior of the lead phosphate particles, with highly variable outcomes (colloidal stabilization or destabilization) possible. In the majority of scenarios tested, including all conditions with low molecular weight river NOM (e.g., SRNOM and UMRNOM), and all NOM types (SRNOM, UMRNOM, PPHA, and LHA) with 100 mM Na⁺, low Ca²⁺ concentration (1 mM), and low NOM concentration (1 mg C/L), the NOM imparted stabilization against aggregation or even induced dissolution or disaggregation, with a distinct “shrinking” observed with PPHA and LHA in 1 mM Ca²⁺. This study specifically delineated the conditions required for rapid aggregation of the particles by NOM, namely the presence of high molecular weight humic acids (e.g., PPHA or LHA) at high concentrations (10 mg C/L) with high concentrations of Ca²⁺ (3 mM). Evaluation of the aggregation behavior of the PPHA and LHA themselves demonstrated that NOM self-interactions largely explain their effects in the different Ca²⁺ concentrations, with low Ca²⁺ resulting in intramolecular bridging, but higher Ca²⁺ resulting in intermolecular bridging. Particle attachment or entrainment in the intermolecularly bridged flocs resulted in even more rapid aggregation. These results suggest that a basic characterization of the NOM (molecular weight and concentration) and Ca²⁺ levels in a given water or soil can be prioritized as important predictors of lead phosphate aggregation and transport behavior.

CHAPTER 5. FUTURE DIRECTIONS

The deposition study in this dissertation mainly focused on column experiments using Ottawa sand as the media. As soil contains multiple constituents, potentially we can investigate deposition behaviors of lead phosphate particles onto other materials, for instance, clay minerals and Fe/Al oxides, which are a representative of the clay fraction in soil.¹⁵³ In contrast to the Ottawa sand used here, Fe/Al oxides are positively charged at neutral pH, so we expect to observe distinct deposition behaviors from current study. Additionally, we can conduct column experiments using Ottawa sand coated with NOM, which is also typical in natural environments. And we can compare the deposition behaviors observed to the findings mentioned in this dissertation where NOM existed in dissolved form. These would be some interesting future directions.

We investigated effects of NOM on aggregation behaviors of lead phosphate particles as discussed in Chapter 4. Since NOM contains multiple functional groups, it could be useful to study aggregation behaviors of lead phosphate in presence of some small molecules with typical and important functional groups. For example, we can select some amino acids including cysteine (thiol functionality), lysine (amine functionality), and serine (hydroxyl functionality). This may help explain the results shown in Chapter 4 using NOM with more complex compositions and functional groups and bring a more comprehensive understanding.

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APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 2

A.1 Natural Organic Matter (NOM) Stock Solution Preparation and Total Organic Carbon (TOC) Measurements

Fulvic acid (Suwannee River) and humic acid (Aldrich) powders were dissolved in ultrapure water (pH = 7.0) and then filtered through a 0.2 μm syringe filter to remove particulate organic matters. The actual total dissolved C concentrations in these filtered stock solutions were determined using total organic carbon (TOC) analyzer (TOC-L, Shimadzu). To start TOC measurements, potassium hydrogen phthalate (KHP) solutions with known carbon concentrations (1, 5, 10, 25, and 50 mg/L) were prepared as standard solutions. Then TOC was determined by treating the samples with phosphoric acid to remove inorganic carbon prior to instrument analysis. According to the TOC measurements, the actual organic carbon contents of the fulvic acid and humic acid in stock solutions were 43 and 3700 mg/L, respectively.

A.2 Scanning Electron Microscopy (SEM) Measurements

SEM measurements (JEOL Ltd.) were performed to characterize of the morphology of aggregates. Particles were let to precipitate and aggregate in 50 mL freshly prepared solutions for 1 h. Then, the precipitation/aggregation solutions were centrifuged at 5,000 rpm for 1 min. After that, the slurry at the bottom was transferred to a clean gold coated silica wafer (Sigma-Aldrich),¹ and was dried in a desiccator. Then the wafer was sputter-coated with gold before SEM measurements. The images were collected at the voltage of 15 kV.

A.3 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) and Raman Spectroscopy Measurements for Phase Identification

As shown in **Table 2.1**, the precipitation solutions were supersaturated with respect to multiple mineral phases. As the amounts of particles formed in solutions were not enough for X-ray diffraction (XRD) measurements, the particles collected from solution were transferred on gold substrates for GIWAXS and Raman measurements, to identify the phases of the particles precipitated in solutions. To prepare enough precipitates for GIWAXS and Raman analysis, 1 L freshly prepared solutions (**Table 2.1**) were sit for 1 h. Then, the precipitates in solutions were collected using centrifugal filters (Amicon-15, Millipore) by centrifuging, and were rinsed with ultrapure water multiple times. After that, the slurry was transferred to a clean gold substrate (Sigma-Aldrich), and was dried in a desiccator overnight before GIWAXS and Raman analysis.

GIWAXS measurements were performed at beamline 12 ID-B of the Advanced Photon Source (APS), Argonne National Laboratory (Argonne, IL). The energy of the synchrotron X-ray radiation was 13.3 keV. The samples were aligned to be parallel with the incident X-ray beam and the substrate was then adjusted vertically to be at the center of the X-ray beam.²⁻⁶ GIWAXS patterns were recorded at an X-ray incidence angle of 0.1° with an exposure time of 1 s. GIWAXS pattern of a clean gold substrate was also collected to provide background scattering data which was subtracted from all GIWAXS scattering data. The obtained scattering curves after background subtraction were plotted as scattering intensity (I) vs. wave vector (q , $\text{\AA}^{-1}$), and were compared with references to identify the mineral phases (**Figure 2.1A**). Detailed information about the Raman spectroscopy measurements can be found in Supporting Information of our previous work.

A.4 Enrichment of Ca^{2+} or Mg^{2+} on Particle Surfaces

For particles precipitated in solutions with the presence of Ca^{2+} and Mg^{2+} , their chemical compositions were measured using ICP-MS to understand the potential enrichment of Ca^{2+} or Mg^{2+} on particle surfaces. To prepare enough precipitates for ICP-MS measurements, 1 L freshly prepared solutions (**Table 2.1**) were sit for 1 h. Then, the precipitates formed in solutions were collected using centrifugal filters (Amicon-15, Millipore) by centrifuging, and were rinsed with ultrapure water multiple times. After that, the particles collected on filters were soaked in 5 mL diluted HNO_3 solution ($\text{pH} = 3$) for 15 min to desorb/dissolve the surface layer of the precipitates. Then, the remaining particles were rinsed with ultrapure water several times and soaked in 5 mL 2% HNO_3 ($\text{pH} = 0.5$) for 24 h to completely dissolve the particles. The dissolved Ca, Mg, Pb and P concentrations were measured by ICP-MS, and atomic ratios of Ca (or Mg) /Pb and Pb/P both on the surface (R_{surface} , desorb/dissolve in $\text{pH} = 3$ HNO_3) and in the lattice of precipitates (R_{lattice} , dissolve in $\text{pH} = 0.5$ HNO_3) were calculated accordingly (**Table A.4**). For both Ca/Pb or Mg/Pb ratios, higher ratios of the surface layer over the lattice were measured, indicating enrichment of both Ca and Mg on lead phosphate particles.

A.5 Comparison of HA/FA Effects on Aggregation

Under the same concentration (0.1 mg C/L), the particle sizes in the presence of fulvic acid were much larger than those in the presence of humic acid, indicating that the retardation effect of humic acid on aggregation was more effective. In Louie et al.'s study, effects of six types of NOM (i.e., Pahokee Peat humic acid, Suwannee River humic acid, Elliott Soil fulvic acid, Pony Lake fulvic acid, Pacific Ocean fulvic acid, Suwannee River NOM) on the aggregation of citrate-stabilized gold nanoparticles were investigated. NOMs

with higher aromaticity and molecular weight were found to have stronger steric repulsion forces.⁷ Here, the molecular weights of fulvic and humic acids were unknown, and humic acid with higher aromaticity can stabilize lead phosphate particles more efficiently than fulvic acid.

A.6 Effects of pH on the Zeta Potential and Aggregation of Particles

In general, zeta potentials of particles decrease with the increase of pH. Therefore, the zeta potential of particles formed under pH 5.5 should be less negatively charged than at pH 7.0 and 8.5. However, zeta potentials of particles measured in the precipitation solutions did not follow this trend, being -38.7 ± 1.0 , -39.1 ± 2.4 and -27.3 ± 3.4 mV at pH = 5.5, 7.0, and 8.5, respectively. In the solution with pH = 5 (set V in **Table 2.1**), the amount of phosphate (i.e., 3.60 mM) was 10 times higher than that at pH = 7 (i.e., 0.32 mM). Therefore, we hypothesized that under pH = 5, more phosphate can adsorb on lead phosphate surfaces, making the zeta potential of lead phosphate to be more negative. To test this hypothesis, the particles were collected from the solutions (**Table 2.1**) and re-dispersed in solutions with pH = 5.5, 7.0 and 8.5 (no Pb^{2+} or PO_4^{3-} ions) for zeta potential measurements. Zeta potential values of these particles at pH 5.5 and 7 followed well with the trend of typical pH titration curves, being -13.6 ± 1.4 and -25.2 ± 5.0 mV, respectively, so our hypothesis was validated.

However, at pH 8.5, the zeta potential of precipitates measured in the absence of lead and phosphate ions was -14.1 ± 1.4 mV, much less negatively charged than that measured at pH 7.0. GWB calculations showed that the precipitation solution was also saturated with respect to cerussite/hydrocerussite at pH = 8.5. Therefore, we hypothesized the potential formation of cerussite/hydrocerussite. However, GIWAXS and Raman

measurement (**Figure 2.1A**) only showed the formation of hydroxylpyromorphite. It is possible that cerussite/hydrocerussite form coatings on hydroxylpyromorphite surfaces changing the zeta potentials, while the amount of cerussite and hydrocerussite as coatings was too few to be detected.

Table A.1. The calculated saturation indices (SI) with respect to Pb-containing minerals under solution conditions of sets I and IV

Set	SI- $\text{Pb}_5(\text{PO}_4)_3\text{OH}$	SI- $\text{Pb}_3(\text{PO}_4)_2$	SI- PbHPO_4	SI- $\text{Pb}(\text{OH})_2$	SI- PbCO_3	SI- $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$
R-1000	12.6	7.5	1.9	-0.3	-0.5	-0.9
R-100	12.6	7.4	1.7	-0.0	-0.2	0.1
I R-60	12.7	7.4	1.6	0.1	-0.1	0.5
R-10	12.7	7.3	1.4	0.5	0.3	1.6
R-1	12.7	7.2	1.3	0.5	0.3	1.6
IS-0.58	12.8	7.5	1.7	0.0	-0.2	0.2
IS-11	12.6	7.3	1.6	0.1	-0.1	0.3
IS-21	12.6	7.3	1.6	-0.0	-0.2	0.0
IV IS-30	12.7	7.4	1.7	-0.0	-0.2	0.0
IS-50	12.7	7.4	1.7	-0.0	-0.2	0.0
IS-80	12.7	7.5	1.8	-0.2	-0.4	-0.4
IS-99	12.7	7.5	1.8	-0.2	-0.4	-0.5

Table A.2. The calculated saturation indices (SI) with respect to Pb-containing minerals under solution conditions of sets II, III and V

	Set	SI ^c - Pb ₅ (PO ₄) ₃ OH	SI ^c - Pb ₃ (PO ₄) ₂	SI ^c - PbHPO ₄	SI- Pb(OH) ₂	SI- PbCO ₃	SI- Pb ₃ (CO ₃) ₂ (OH) ₂	SI-others
II	1.2 mM Ca(NO ₃) ₂	12.6	7.3	1.6	0.1	-0.2	0.2	SI- Ca ₅ (PO ₄) ₃ OH = 7.7 SI-Ca ₃ (PO ₄) ₂ = 0.9
	1.2 mM Mg(NO ₃) ₂	12.6	7.3	1.6	0.1	-0.1	0.3	N/A
	3.6 mM NaCl	12.7	7.4	1.7	-0.0	-0.2	0.1	SI- Pb ₅ (PO ₄) ₃ Cl = 24.9
	3.2 mM NaF	12.6	7.3	1.6	0.1	-0.2	0.3	N/A
	3.1 mM NaHCO ₃	12.6	7.3	1.6	0.0	1.2	3.0	N/A
III	1.2 mM CaCl ₂ (0.1 – 5 mg C/L FA, 0.05 – 5 mg C/L HA)	12.6	7.3	1.6	0.1	-0.1	0.3	SI- Pb ₅ (PO ₄) ₃ Cl = 24.6 SI- Ca ₅ (PO ₄) ₃ OH = 7.8 SI-Ca ₃ (PO ₄) ₂ = 0.9
V	pH-5.5	12.6	7.9	2.7				
	pH-8.5	12.6	6.9	0.7	1.4	1.2	4.4	N/A

Table A.3. Solution conditions and zeta potentials of precipitation experiments with varied aqueous Mg/Ca concentrations

	Pb ²⁺ , μM	PO ₄ ³⁻ , mM	NO ₃ ⁻ , mM	Na ⁺ , mM	Ca ²⁺ , mM	Mg ²⁺ , mM	IS ^a , mM	pH ^b	SI ^c	ξp ^d , mV
1	2.70	0.27	3.21	3.47	0.1	0	4	7.0	12.4	-32.1 ± 1.3
2	2.90	0.29	2.81	2.30	0.5	0	4	7.0	12.5	-20.8 ± 0.6
3	2.80	0.28	2.61	1.50	0.8	0	4	7.1	12.4	-16.6 ± 0.5
4	2.70	0.27	3.21	3.47	0	0.1	4	7.0	12.4	-33.0 ± 1.6
5	2.90	0.29	2.81	2.30	0	0.5	4	7.0	12.5	-22.7 ± 0.5
6	2.80	0.28	2.61	1.50	0	0.8	4	7.1	12.4	-15.6 ± 1.8

Note: IS^a: Ionic Strength. pH^b: GWB calculated pH values. SI^c: Saturation indices with respect to hydroxyporomorphite, which was fixed to 12.4 ± 0.1. SI = Log (Q/K_{sp}), where Q is the actual dissolved composition, and $K_{sp}(\text{hydroxyporomorphite}) = 10^{-62.79}$ at 20°C was used for SI calculations based on GWB database. ξp^d: zeta potentials of particles measured in precipitation solutions.

Table A.4. Chemical compositions of precipitates formed in the presence of Ca/Mg measured by ICP-MS

	R _{surface}	R _{lattice}
Ca/Pb	41.39	0.71
Mg/Pb	0.46	0.09

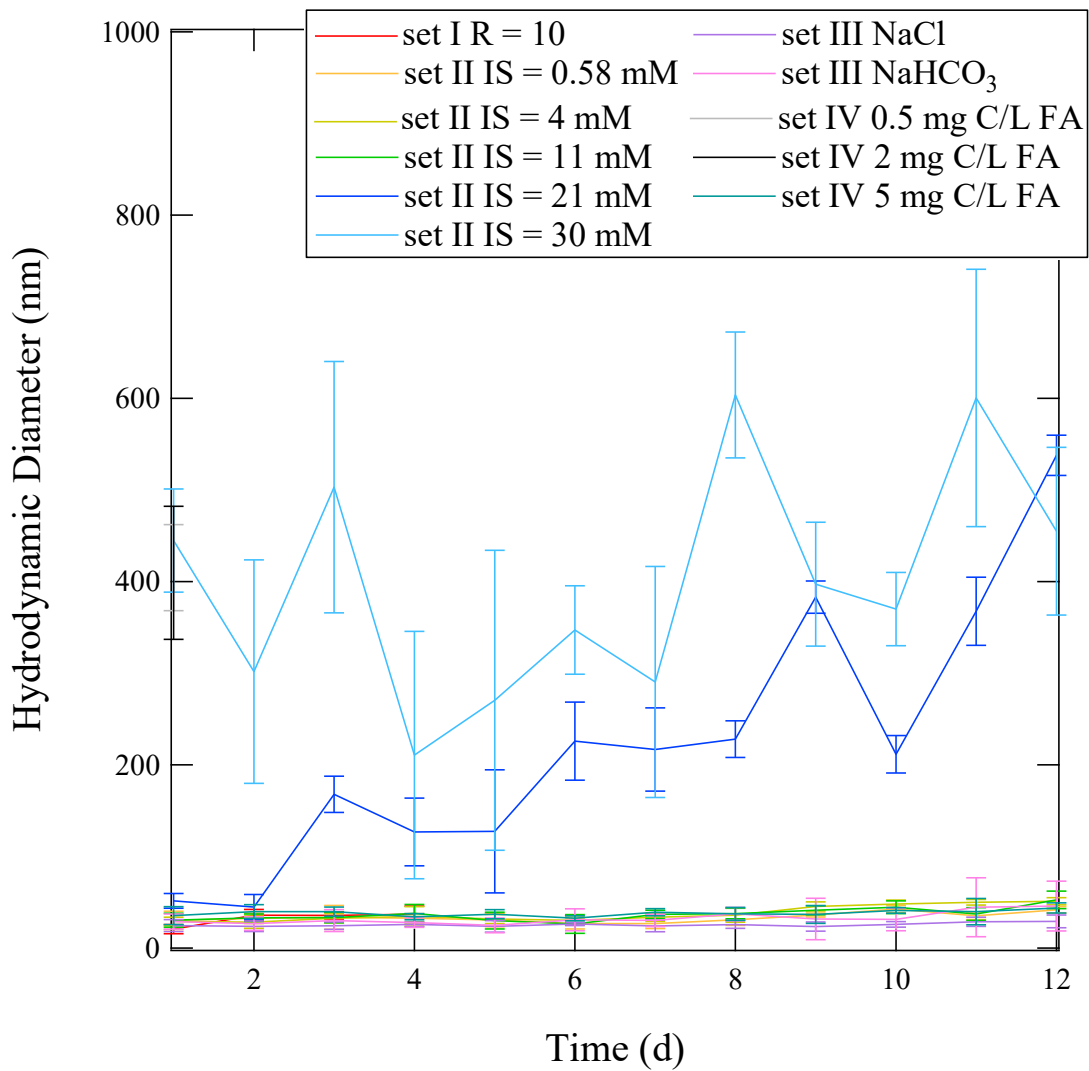


Figure A.1. Long-term size evolutions of lead phosphate particles under varied aqueous conditions measured by DLS.

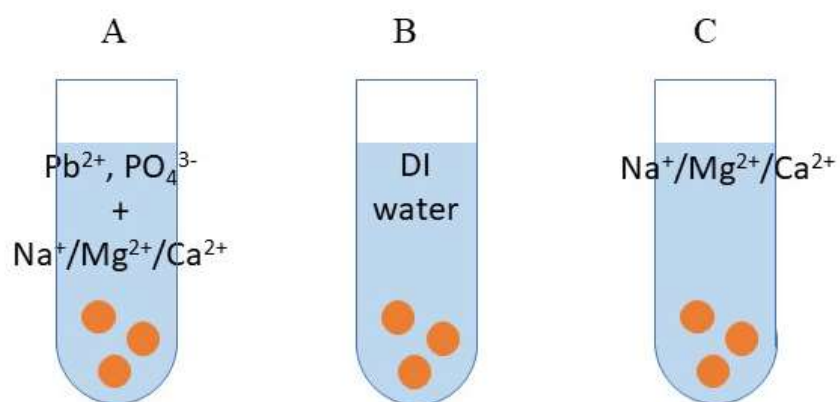


Figure A.2. Illustration of zeta potential measurements of particles in (A) precipitation solution, (B) ultrapure water with pH adjusted to the same as precipitation experiments, and (C) salt solutions without lead or phosphate ions.

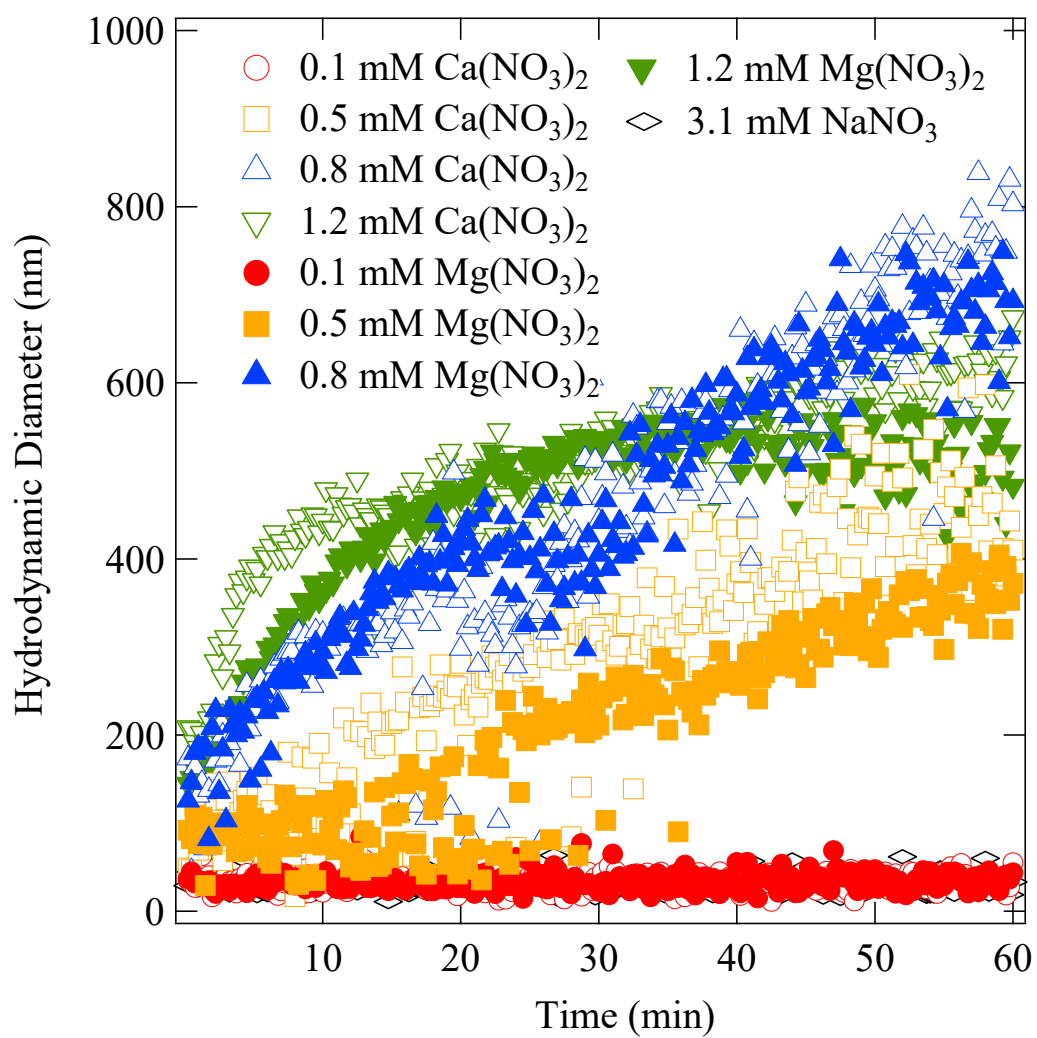


Figure A.3. Size evolutions of particles in the presence of cations measured by DLS.

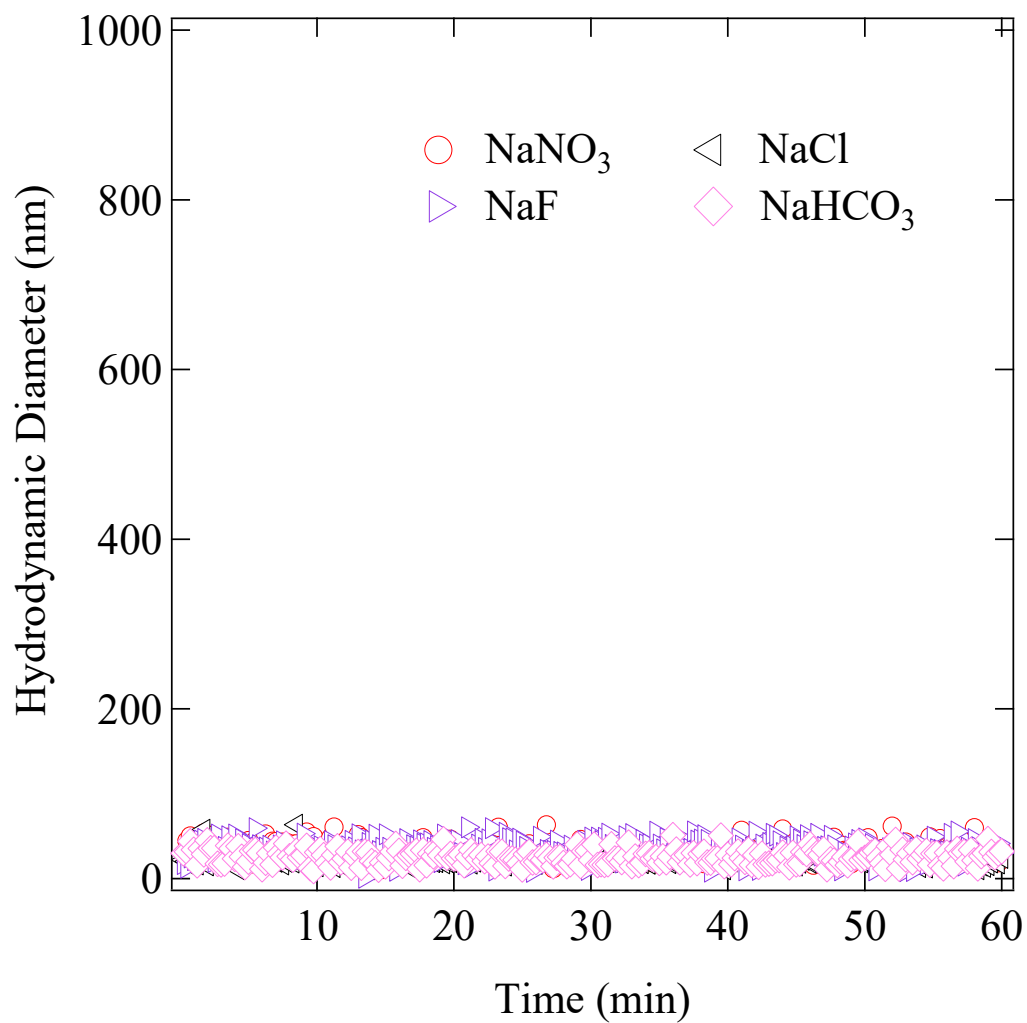


Figure A.4. Size evolutions of particles in the presence of anions measured by DLS.

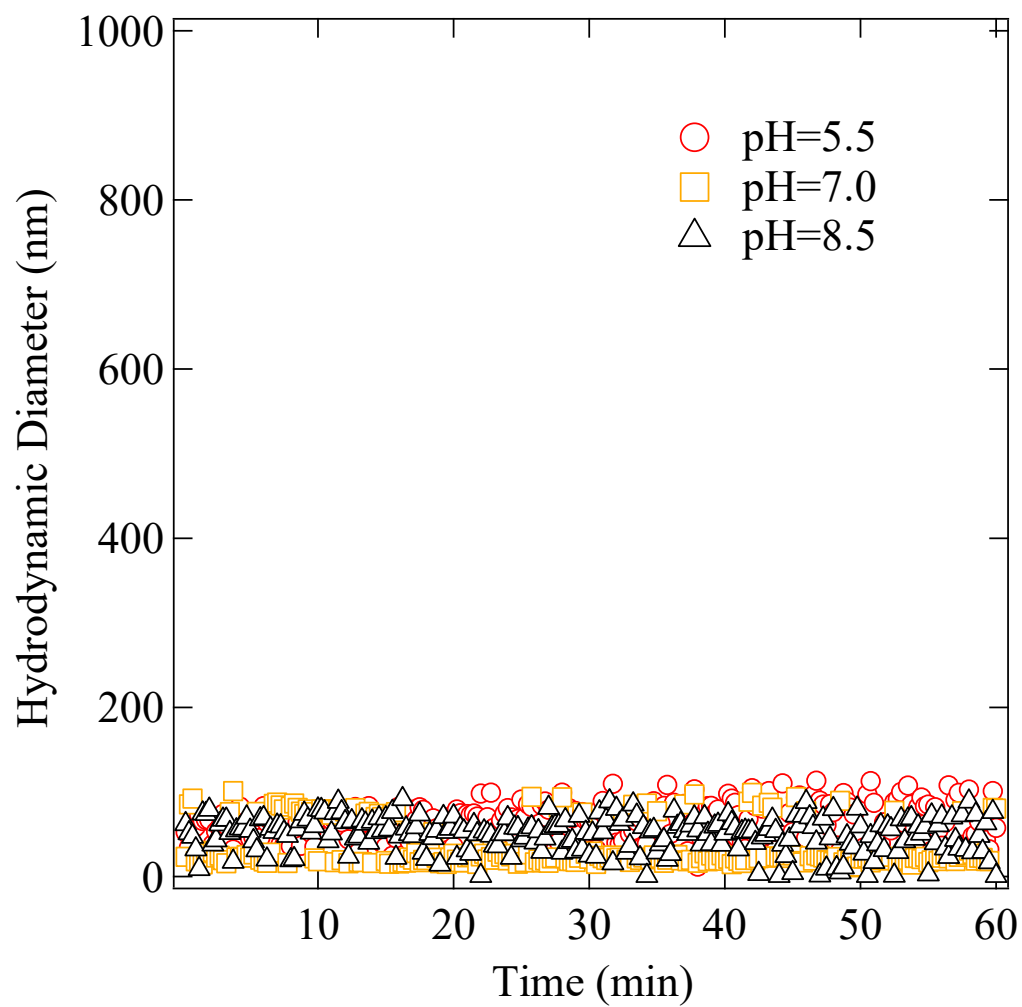


Figure A.5. Size evolutions of particles formed under varied pH as measured by DLS.

APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER 3

B.1 Humic Acid (HA) Stock Solution Preparation and Total Organic Carbon (TOC) Measurements

Humic acid (Sigma Aldrich, St. Louis, MO) powders were dissolved by adding 3 g to 250 mL of ultrapure water. The HA solution was adjusted to pH 7.0 using 1 M NaOH and then filtered through a 0.45 μm polyethersulfone (PES) syringe filter (Express Plus, Merck Millipore, Carrigtwohill Co., Cork, Ireland) to remove the undissolved portion. The C concentration of the filtered stock solution was measured using a TOC analyzer (TOC-L, Shimadzu, Columbia, MD). Phosphoric acid was used for inorganic carbon removal, and the TOC oxidation was performed on a Pt catalyst heated at 680 $^{\circ}\text{C}$. A series of standard solutions (0, 0.5, 1, 2, 5, 10, 50, and 100 mg C/L potassium hydrogen phthalate) was prepared to develop a calibration curve. The humic acid stock solution was diluted to fall within the calibration range for measurement, and the original concentration of the humic acid stock solution was measured to be 3049 mg C/L.

B.2 Sand Column Preparation for Column Experiments

B.2.1 Determination of Porosity

The chromatographic column was packed with dry sand. The height and internal diameter of the sand column were measured to compute the volume occupied by the bulk sand. The weight of the dry packed glass column was also measured. Then, the column was cleaned and packed with wet sand to the same height as when packed using dry sand and the total weight was measured. The porosity (η) was calculated as: $\eta = [(\text{weight of wet}$

sand – weight of dry sand) / density of water] / volume of sand column, being 0.40 ± 0.01 for the duplicates.

B.2.2 Column Packing Procedure

Approximately 40 g of sand was added to a beaker containing 20 mL of ultrapure water. A small amount (~ 2 mL) of water was added to the glass column, and then the wet sand was added to the column in small increments (~ 1 cm each time). The column was uniformly packed and no air bubbles were trapped. After packing, the glass column was covered with nylon mesh (150 μm) on top, sealed with Teflon tape, screw-capped and further sealed with Parafilm.

B.2.3 Breakthrough Curve Modeling

CXTFIT fitting was performed by Daniel Bao in STANMOD Suite v. 2.08.¹⁵⁴ The settings used were dimensionless parameters, step boundary conditions with a dimensionless concentration of $C/C_0 = 1$ applied starting at time zero, and zero initial value and zero production conditions. Only the data up to the first 10 pore volumes (PV) of injection were evaluated (before the wash-out step from 10 to 16 PV). The dimensionless dispersion number, i.e., the inverse Peclet number $1/\text{Pe} = D/u_x L$ (where D is the dispersion coefficient (L^2/T), u_x is the linear velocity (L/T), and L is the column length (L)) was first fitted for the inert tracer (NaBr) data assuming no retardation (i.e., retardation factor $R = 1$) and no reactive or other loss (i.e., dimensionless decay coefficient, $\mu^E = 0$). Note that the first-order decay coefficient, μ , is computed as

$$\mu = \mu_l + \frac{\rho_b K_d \mu_s}{\theta}, \quad (\text{B.1})$$

where θ is the volumetric water content (L^3/L^3), μ_l is the first-order decay coefficient in the liquid phase, μ_s is the first-order decay coefficient in the adsorbed phase, ρ_b is the soil bulk density (M/L^3), K_d is an empirical distribution constant (L^3/M).¹⁵⁴ μ^E , the dimensionless decay coefficient, is expressed as

$$\mu^E = \frac{L(\theta\mu_l + \rho_b K_d \mu_s)}{\theta u_x}. \quad (B.2)$$

Assuming μ_l and μ_s are identical, then Equation B.1 can be reduced to $\mu = \mu_l R$, given by

$$R = 1 + \frac{\rho_b K_d}{\theta}. \quad (B.3)$$

Then Equation B.2 can be simplified accordingly.

Fitted results are shown in **Figure B.1** and yielded a best-fit dispersion number of 0.143.

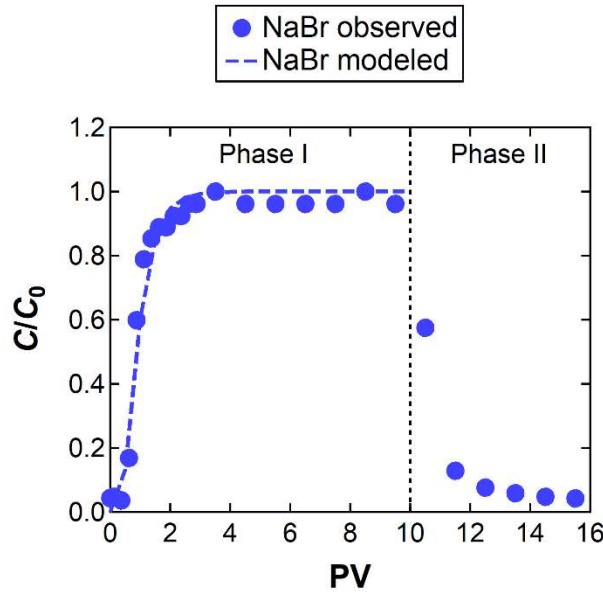


Figure B.1. Breakthrough curve of tracer (NaBr) and best fit result from CXTFIT (fitted dispersion number, with fixed dimensionless velocity of 1, retardation factor of 1, and decay coefficient of 0).

For the lead phosphate particle deposition data, CXTFIT was applied fixing the dimensionless velocity to 1 and dispersion number to 0.143 from the tracer test. Particle deposition data were fitted for total and $> 0.1 \mu\text{m}$ lead profiles for freshly prepared and aged suspensions. Data were only fitted prior to the occurrence of any observed ripening (note, the fitted results are only taken as a rough estimate when few data points were available) to fit R and μ . Because R was similar across all ionic strengths for the same condition (e.g., total lead for freshly prepared suspensions), the fitting was also conducted with R fixed to that fitted on the 5 mM sample and fitting only μ to reduce the number of fitting parameters; results were similar with either approach. Finally, the fitted values were used to extrapolate a predicted breakthrough across the entire range of 0 to 10 PV, assuming no ripening or blocking interactions.

B.3 Saturation Indices (SI) and Phase Identification by X-ray diffraction (XRD) Analysis for Samples Prepared for the Deposition Experiments

Table B.1. The calculated saturation indices (SI) with respect to Pb-containing minerals with varied ionic strength (IS) and P/Pb ratio ($R_{P/Pb}$)

Set	SI- $Pb_5(PO_4)_3OH$	SI- $Pb_3(PO_4)_2$	SI- $PbHPO_4$	SI- $Pb(OH)_2$	SI- $PbCO_3$	SI- $Pb_3(CO_3)_2(OH)_2$
IS 5 mM	21.1	12.6	3.6	1.4	1.2	4.2
IS 10 mM	21.2	12.6	3.5	1.5	1.3	4.5
I ^a IS 12.5 mM	21.1	12.5	3.5	1.5	1.3	4.6
IS 15 mM	21.2	12.6	3.5	1.5	1.3	4.5
IS 20 mM	21.2	12.6	3.5	1.4	1.2	4.4
II $R_{P/Pb} = 1$	21.1	12.4	3.2	1.9	1.7	5.7

Note: I^a: $R_{P/Pb} = 10$.

Table B.2. The calculated saturation indices (SI) with respect to Pb-containing minerals in presence of Ca^{2+} and NOM

Set	SI ^c - Pb ₅ (PO ₄) ₃ OH	SI ^c - Pb ₃ (PO ₄) ₂	SI ^c - PbHPO ₄	SI- Pb(OH) ₂	SI- PbCO ₃	SI- Pb ₃ (CO ₃) ₂ (OH) ₂	SI-others	
III ^a	0.2 mM Ca(NO ₃) ₂	21.2	12.6	3.5	1.5	1.3	4.6	SI- Ca ₅ (PO ₄) ₃ OH = 5.1
								SI- Ca ₅ (PO ₄) ₃ OH = 8.5
	1 mM Ca(NO ₃) ₂	21.1	12.5	3.5	1.5	1.3	4.6	SI- Ca ₃ (PO ₄) ₂ = 1.4
								SI- Ca ₄ H(PO ₄) ₃ 3H ₂ O = 0.5
								SI- CaHPO ₄ = 0.1
IV ^a	0.2 mM Ca(NO ₃) ₂ (0.05 – 5 mg C/L HA)	21.2	12.6	3.5	1.5	1.3	4.6	SI- Ca ₅ (PO ₄) ₃ OH = 5.1

Note: III^a, IV^a: $R_{\text{P/Pb}} = 10$.

B.4 Determination of Critical Coagulation Concentration (CCC)

The size evolution of particles formed under varied ionic strength are shown in **Figure B.2a**. Given the rapid aggregation in many cases (first measured size, $D_1 \gg 1.3 \times$ initial particle size, D_0), a linear rate in the dimer formation regime could not be calculated. Instead, aggregation rates k were computed between the initial particle size and first particle size measured.¹⁵⁵¹⁵⁵ The attachment efficiency can then be calculated as k/k_{fast} , where k_{fast} is the maximum, diffusion-limited aggregation rate observed in the experiments. The attachment efficiency as a function of IS was plotted on a log-log plot (**Figure B.2b**), and the CCC was determined to be 99 mM from the intersection of the line of best fit with attachment efficiency of 1.

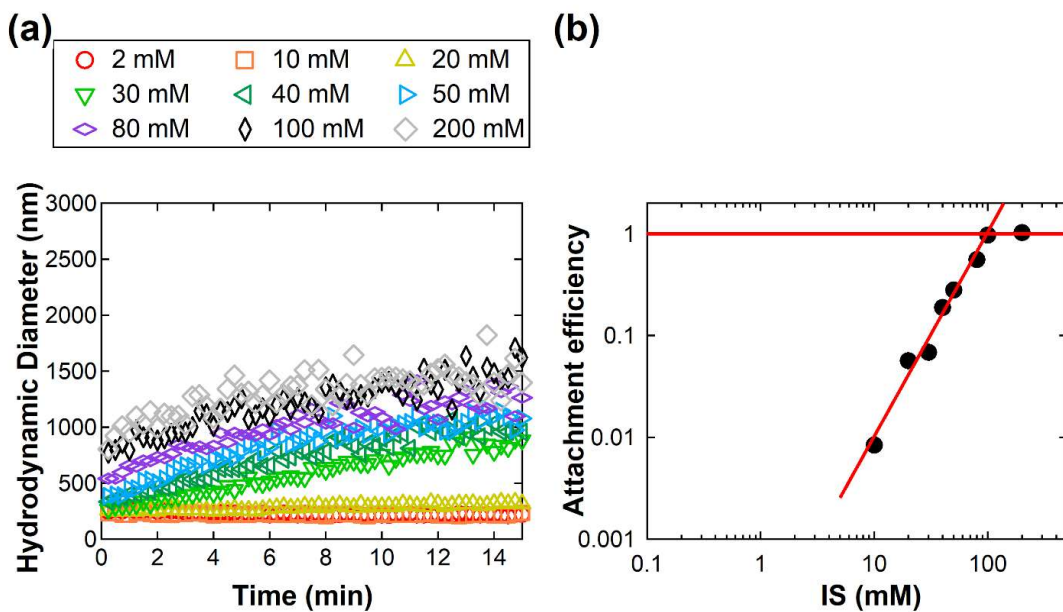


Figure B.2. Size evolutions of lead phosphate particles within 15 min measured by dynamic light scattering (DLS) (a), and log-log plot of attachment efficiency versus IS for determination of the experimental CCC value (b).

B.5 Zeta Potentials of Lead Phosphate Particles for the Homoaggregation Experiments Used for CCC Determination

Figure B.3 presents the experimental (measured) zeta potentials of the lead phosphate particles under ionic strengths used for the CCC evaluation and DLVO modeling hereafter.

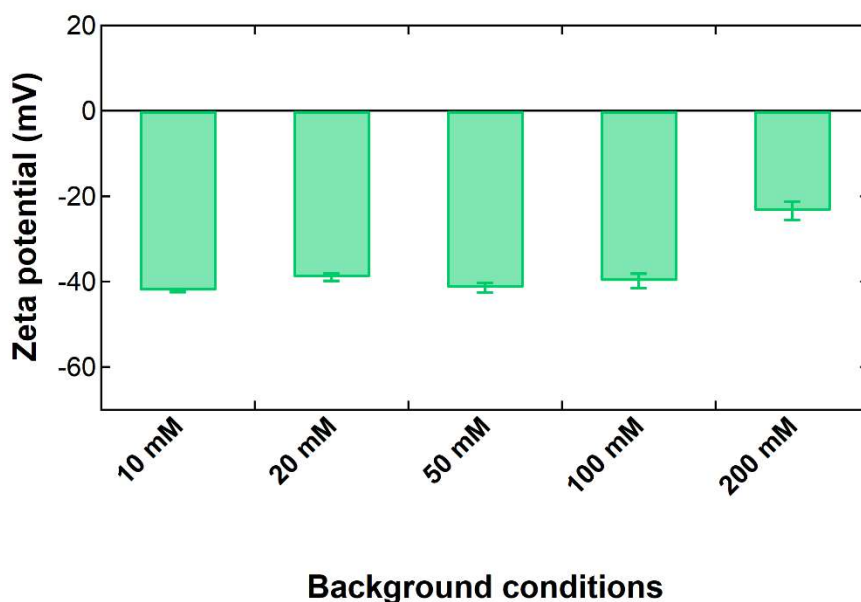


Figure B.3. Zeta potential of lead phosphate particles under varied IS in the homoaggregation experiments for CCC determination and Hamaker constant estimation.

B.6 Estimation of the CCC of Lead Phosphate Particles and Their Hamaker Constant in Water

The Hamaker constant of lead phosphate has not been reported before. In this study, the Hamaker constant, A_{131} , of the particles (material “1”) interacting across water (material “3”) was estimated from the homoaggregation measurements using DLVO theory:¹⁵⁶

$$V_T = V_{EDL} + V_{VDW}, \quad (B.4)$$

$$V_{EDL} = 64\pi\epsilon_0\epsilon_r \left(\frac{a_p}{2}\right) \left(\frac{k_B T}{e}\right)^2 \left(\tanh \frac{e\psi_p}{4k_B T}\right)^2 \exp(-\kappa h), \quad (B.5)$$

$$\kappa = \sqrt{\frac{2N_A e^2 (IS)}{\epsilon_0 \epsilon_r k_B T}}, \quad (B.6)$$

$$\text{and} \quad V_{VDW} = -\frac{A_{131} a_p}{12h(1+14h/\lambda)} \quad (B.7)$$

where V_T is the total potential energy, V_{EDL} is the electrostatic repulsive energy, V_{VDW} is the van der Waals attractive energy, ϵ_0 is the permittivity of vacuum ($8.85 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$), ϵ_r is the dielectric constant of water (78.54 at 25 °C), a_p is the radius of the spherical particle (nm), k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), T is temperature (K), e is the elementary electric charge ($1.60 \times 10^{-19} \text{ C}$), ψ_p is the surface potential of the nanoparticles (V), κ is the Debye constant (nm^{-1}), h is the distance between the nanoparticles (nm), IS is the ionic strength of the monovalent electrolyte ($\text{mol} \cdot \text{m}^{-3}$), N_A is the Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$), and λ is a characteristic wavelength (typically around 100 nm).¹¹⁵ Here, ψ_p was estimated as the measured zeta potential at each IS in the homoaggregation experiments (**Figure B.2**).

At the CCC, there should be no energy barrier to attachment, i.e., $V_T = 0$ at any distance ($h > 0$). Hence, A_{131} was adjusted until the energy barrier was zero at the experimental CCC of $\approx 100 \text{ mM}$ (as determined in **Figure B.2**). The A_{pwp} to achieve this condition was $3.0 \times 10^{-20} \text{ J}$, and the corresponding interaction energy profiles are shown in **Figure B.4**. Note a secondary energy minimum is predicted at 100 mM as well as lower ionic strengths, and hence attachment in the secondary minimum could have influenced the experimental homoaggregation results in **Figure B.2**. However, the estimated A_{pwp} of 3.0

$\times 10^{-20}$ J is of a reasonable value compared to other reported Hamaker constants for inorganic materials interacting across water.¹¹¹

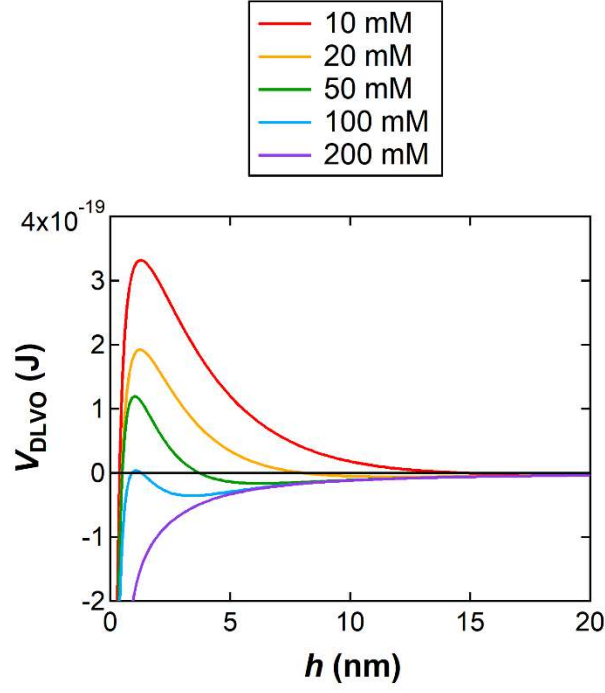


Figure B.4. DLVO energy profile used to estimate A_{131} as that which eliminates the energy barrier at the CCC of ≈ 100 mM.

The Hamaker constant for the lead phosphate interacting over vacuum, A_{11} , is required later to compute the Hamaker constant for interaction with sand collectors in the deposition studies and can be determined by applying

$$A_{131} = (A_{11}^{1/2} - A_{33}^{1/2})^2, \quad (\text{B.8})$$

where A_{33} is 2.43×10^{-20} J for water.¹¹⁴ Hence, $A_{11} \approx 1.1 \times 10^{-19}$ J for lead phosphate interacting over vacuum.

B.7 Breakthrough and Retention Profiles of $< 0.1 \mu\text{m}$ and $> 0.1 \mu\text{m}$ Lead Under Varied Ionic Strengths Using Monovalent Electrolyte

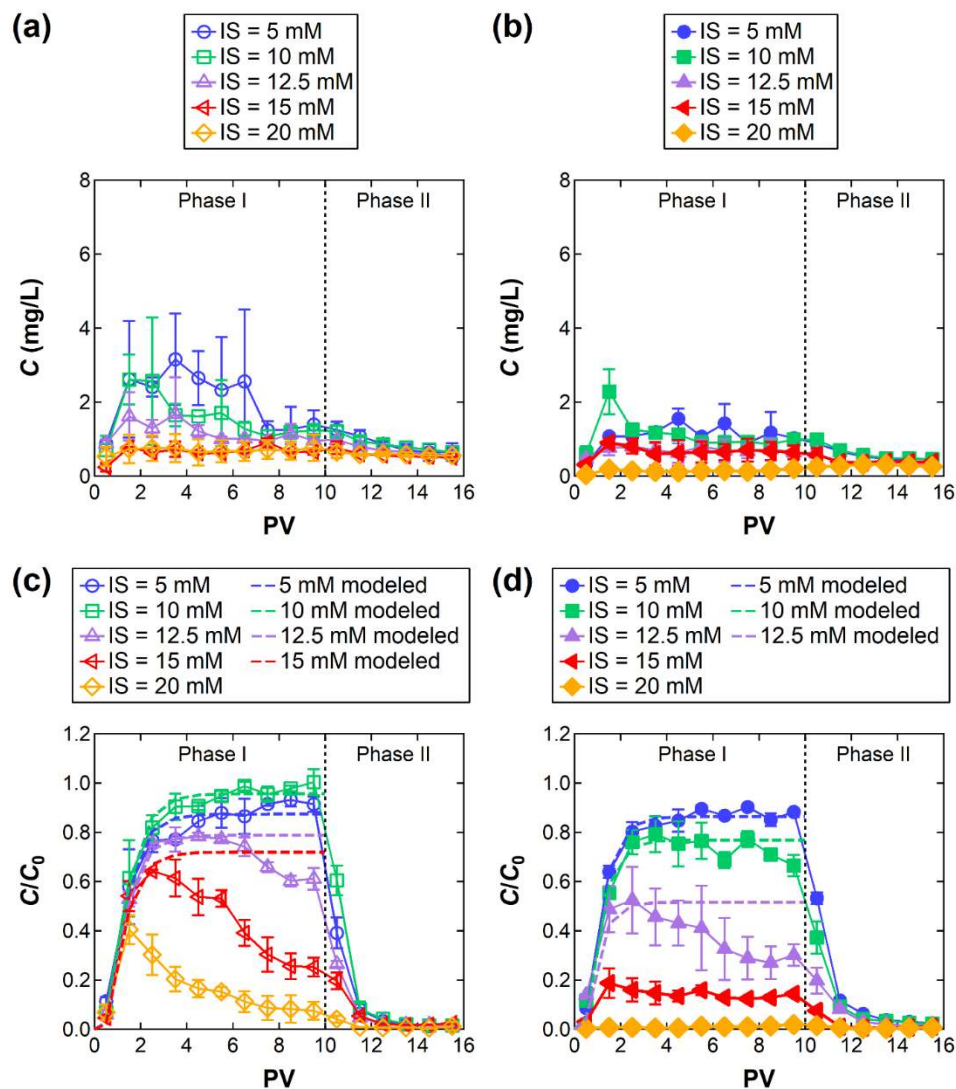


Figure B.5. Breakthrough curves of $< 0.1 \mu\text{m}$ lead under IS 5 - 20 mM for fresh suspensions (a) and aged suspensions (b). Breakthrough curves of $> 0.1 \mu\text{m}$ lead and fitting results using CXTFIT for fresh suspensions (c) and aged suspensions (d).

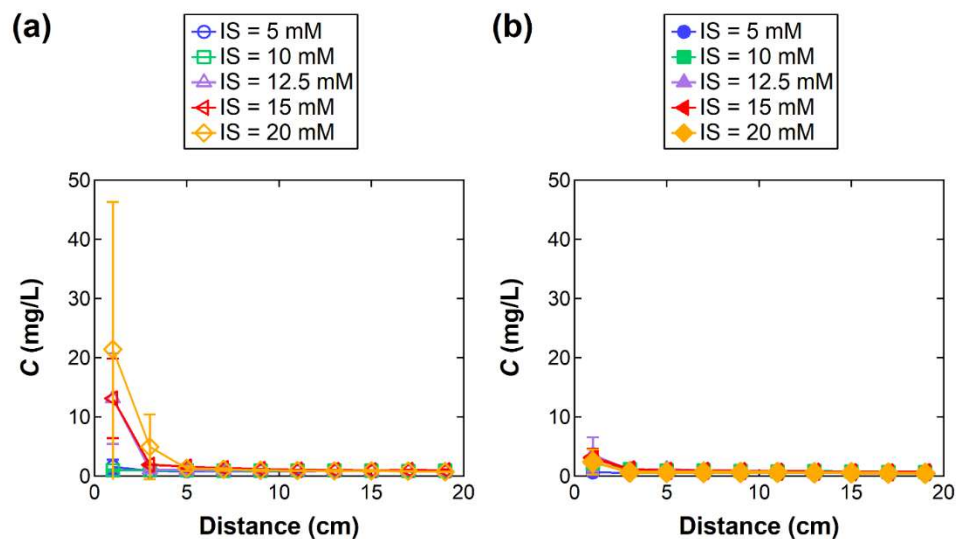


Figure B.6. Retention profiles of lead under varying IS (5 to 20 mM) for fresh suspensions (a) and aged suspensions (b), as measured in the sectioned sand after the deposition experiments.

B.8 Recoveries computed from the mass balance

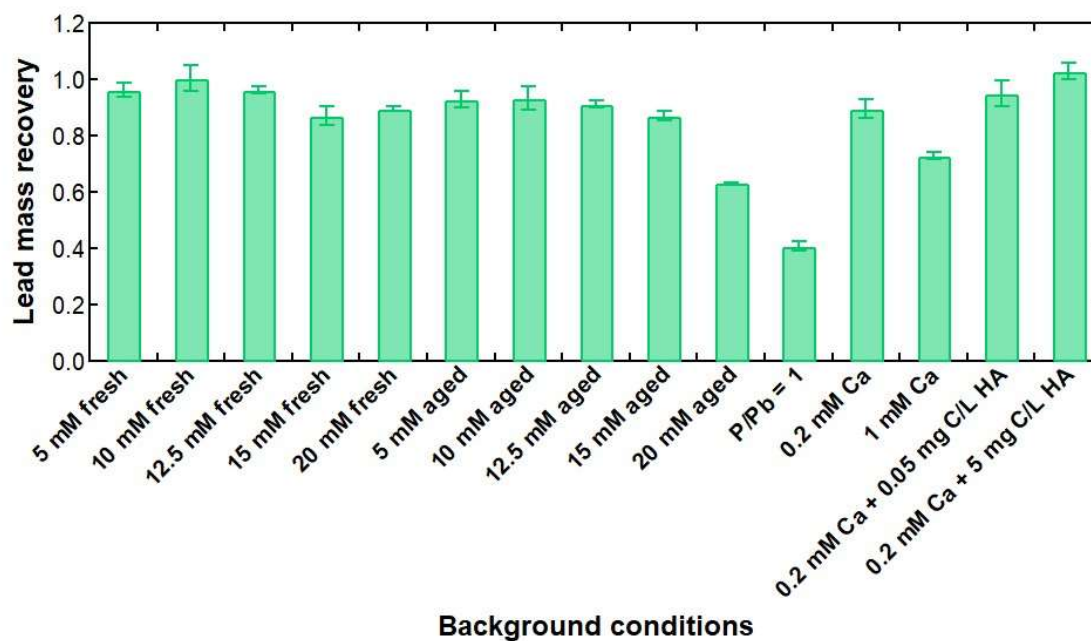


Figure B.7. Recoveries computed from the mass balance.

B.9 Application of Colloid Filtration Theory (CFT) and DLVO Theory to Predict Critical Deposition Concentration (CDC) in the Absence of Ripening, Blocking, or Straining

B.8.1 Prediction of CDC from DLVO Theory

Similarly to the CCC analysis, the CDC for the lead phosphate – sand attachment can be estimated using DLVO theory. Assuming the physical dimension of the sand is large relative to the lead phosphate particles, a sphere-plate interaction can be estimated and the electrostatic and van der Waals interaction energies can be modeled using

$$V_{EDL} = 64\pi\epsilon_0\epsilon_r(a_p)\left(\frac{k_B T}{e}\right)^2 \left(\tanh \frac{e\psi_p}{4k_B T}\right) \left(\tanh \frac{e\psi_s}{4k_B T}\right) \exp(-\kappa h) \quad (B.9)$$

and
$$V_{VDW} = -\frac{A_{132}a_p}{6h(1+14h/\lambda)}, \quad (B.10)$$

where ψ_s is the surface potential of the sand collectors (mV) as measured on the sand colloids, A_{132} is the overall Hamaker interaction parameter, A_{132} , for the deposition of particle (“1”) onto sand collector (“2”) interacting across water (“3”).¹⁵⁶ All other parameters are defined with Equations B.4 to B.7. A_{132} was estimated using

$$A_{132} = (A_{11}^{1/2} - A_{33}^{1/2})(A_{22}^{1/2} - A_{33}^{1/2}), \quad (B.11)$$

where A_{ii} is the Hamaker constant of the material “ i ” interacting with itself over vacuum.¹⁵⁷ A_{22} is taken as 6.5×10^{-20} J for silica,¹¹¹ and A_{11} for lead phosphate and A_{33} for water as reported earlier in the Hamaker constant determination. A_{132} was hence calculated to be 1.7×10^{-20} J.

At the CDC, the energy barrier for primary deposition diminishes to zero at all distances ($h > 0$). Hence, given the computed interaction energy profiles at several ionic

strengths, the CDC was estimated to fall between 100 and 150 mM (**Figure B.8a**). However, a secondary minimum was also observed (**Figure B.8b**) with a depth of ≈ 3.8 $k_B T$ at 50 mM IS, and hence weak attachment in this secondary minimum can also occur at lower ionic strengths.

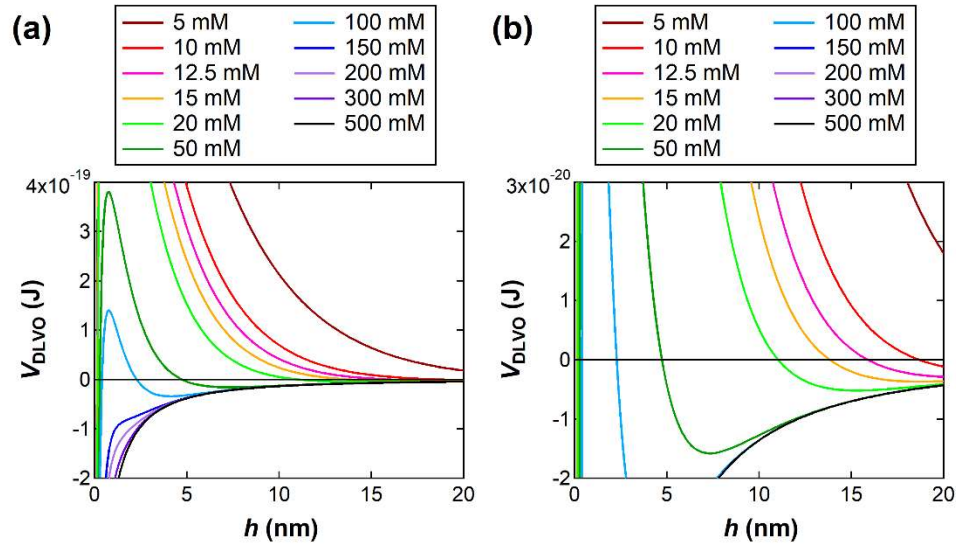


Figure B.8. DLVO interaction energy profiles computed for the lead phosphate particle – sand interaction at various ionic strengths as monovalent electrolyte (a), with presence of secondary minimum emphasized in (b).

B.8.2 Empirical Determination of Attachment Efficiency

Given experimental data on C/C_0 from column deposition experiments and other physical parameters of the particles, sand, and column experiment, an empirical attachment efficiency, α , can be calculated by applying clean-bed CFT using

$$\alpha = -\frac{2d_c}{3(1-\varepsilon)\eta_0 L} \ln\left(\frac{C}{C_0}\right), \quad (\text{B.12})$$

where d_c is the collector diameter, ε is the porosity, η_0 is the single collector efficiency, L is the length of the column, C is the column effluent particle concentration when the

breakthrough curve reaches a plateau, and C_0 is the influent particle concentration.¹⁵⁸ η_0 can be estimated using the correlation equation as

$$\eta_0 = 2.4A_S^{\frac{1}{3}}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdW}^{0.052} + 0.55A_SN_R^{1.675}N_A^{0.125} + 0.22N_R^{-0.24}N_G^{1.11}N_{vdW}^{0.053} . \quad (\text{B.13})$$

All dimensionless parameters are defined in the work of Tufenkji and Elimelech.¹⁵⁹

Given Equations B.12 and B.13, η_0 and the empirical values of α were computed for the freshly prepared particles using the extrapolated C/C_0 from the CXTFIT results (**Figure 3.2a** and **Figure B.5a**). Computed η_0 values were listed in **Table B.3**. A log-log plot of the empirical attachment efficiency vs. IS can then be used to estimate the critical deposition concentration (CDC), where attachment efficiency reaches 1 (**Figure B.9**). Note there were only a limited range of IS where the C/C_0 could be extrapolated and showed a decreasing trend with IS, so this analysis is only presented as a rough estimate to estimate a CDC for order-of-magnitude comparison against that predicted hereafter.

Table B.3. Computed single collector efficiencies

IS (mM)	10	12.5	15
η_0	0.009556	0.009098	0.008988

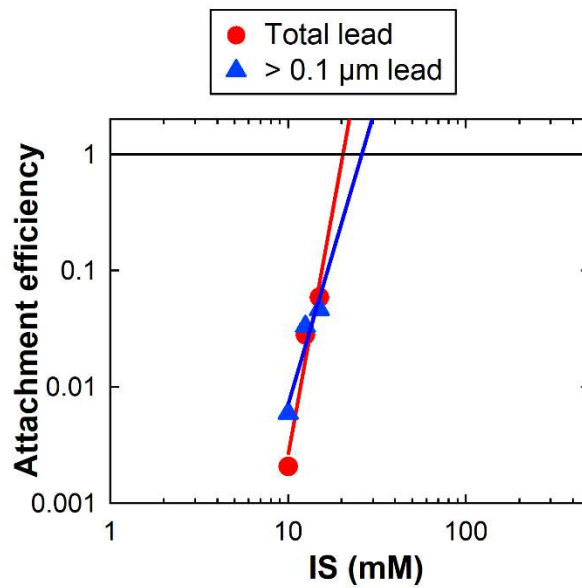
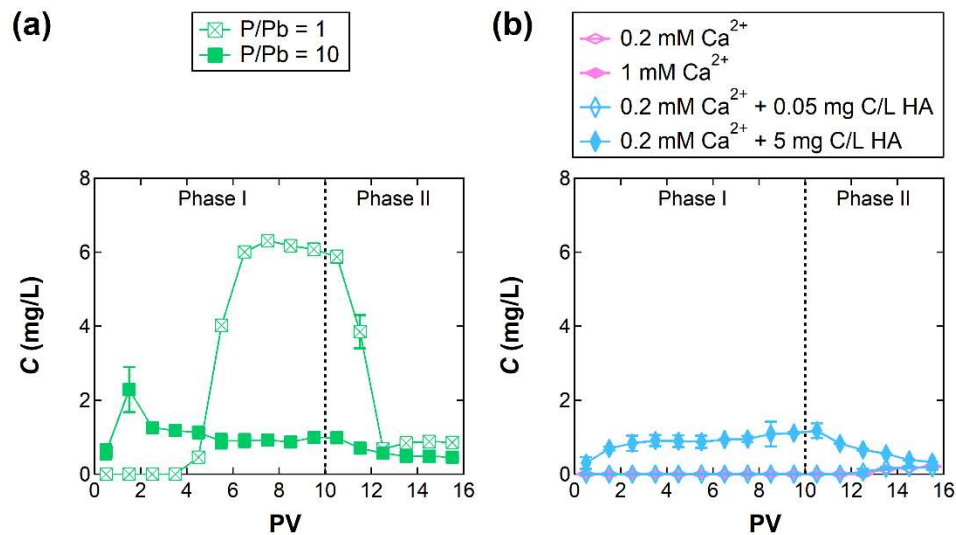


Figure B.9. Empirical CDC determination, with attachment efficiencies estimated using the extrapolated C/C_0 from the initial portion of the breakthrough curves for deposition of fresh suspensions, either for the total lead or $> 0.1 \mu\text{m}$ lead.

B.10 Breakthrough and Retention Profiles of $< 0.1 \mu\text{m}$ and $> 0.1 \mu\text{m}$ Lead Under Varied Phosphate to Lead Ratios ($R_{\text{P/Pb}}$), or in the Presence of Ca^{2+} With or Without HA



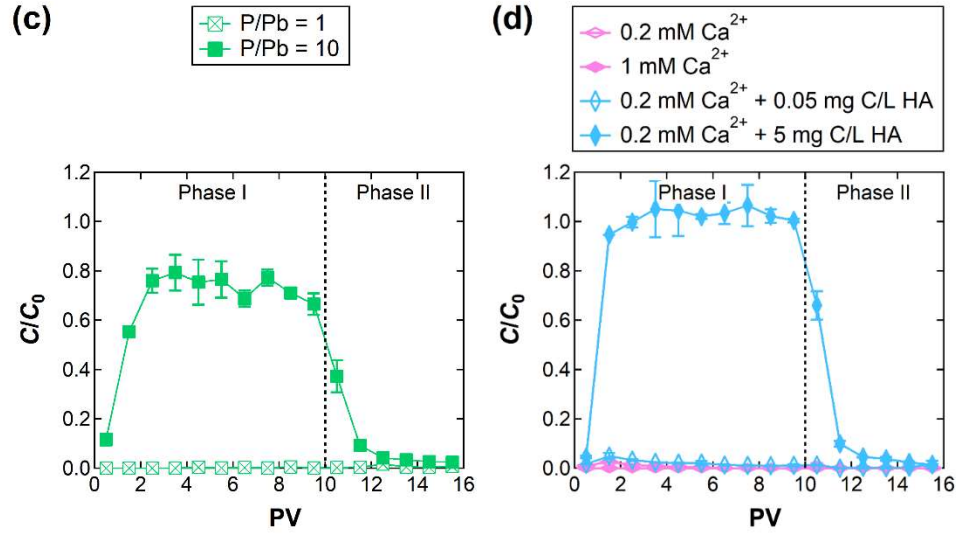


Figure B.10. Breakthrough curves of $< 0.1 \mu\text{m}$ lead under $R_{P/Pb} = 1$ and 10 (a), or in the presence of Ca^{2+} with or without varying concentrations of HA (b), and breakthrough curves of $> 0.1 \mu\text{m}$ lead (c,d) for the same conditions.

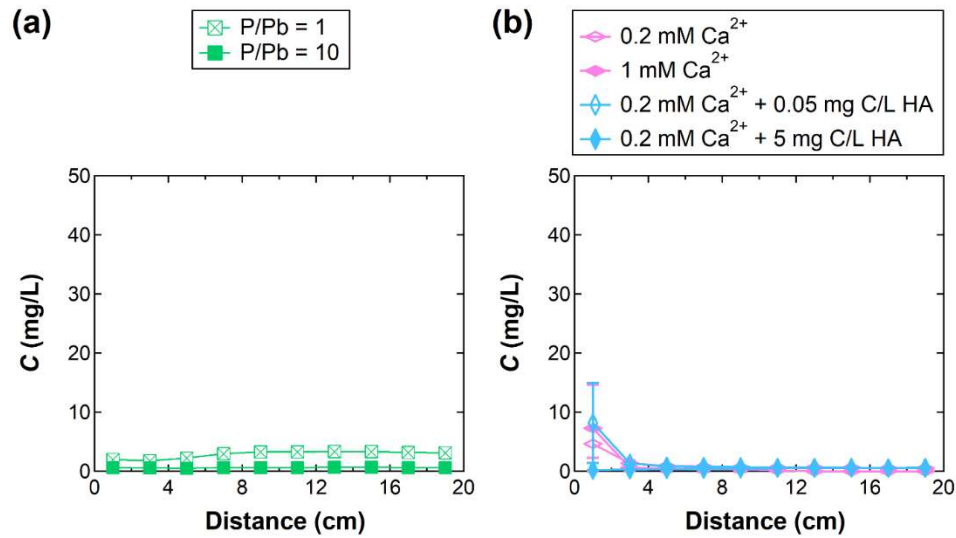


Figure B.11. Retention profiles of lead under $R_{P/Pb} = 1$ and 10 (a), or in the presence of Ca^{2+} with or without varying concentrations of HA (b), as measured in the sectioned sand after the deposition experiments.

APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 4

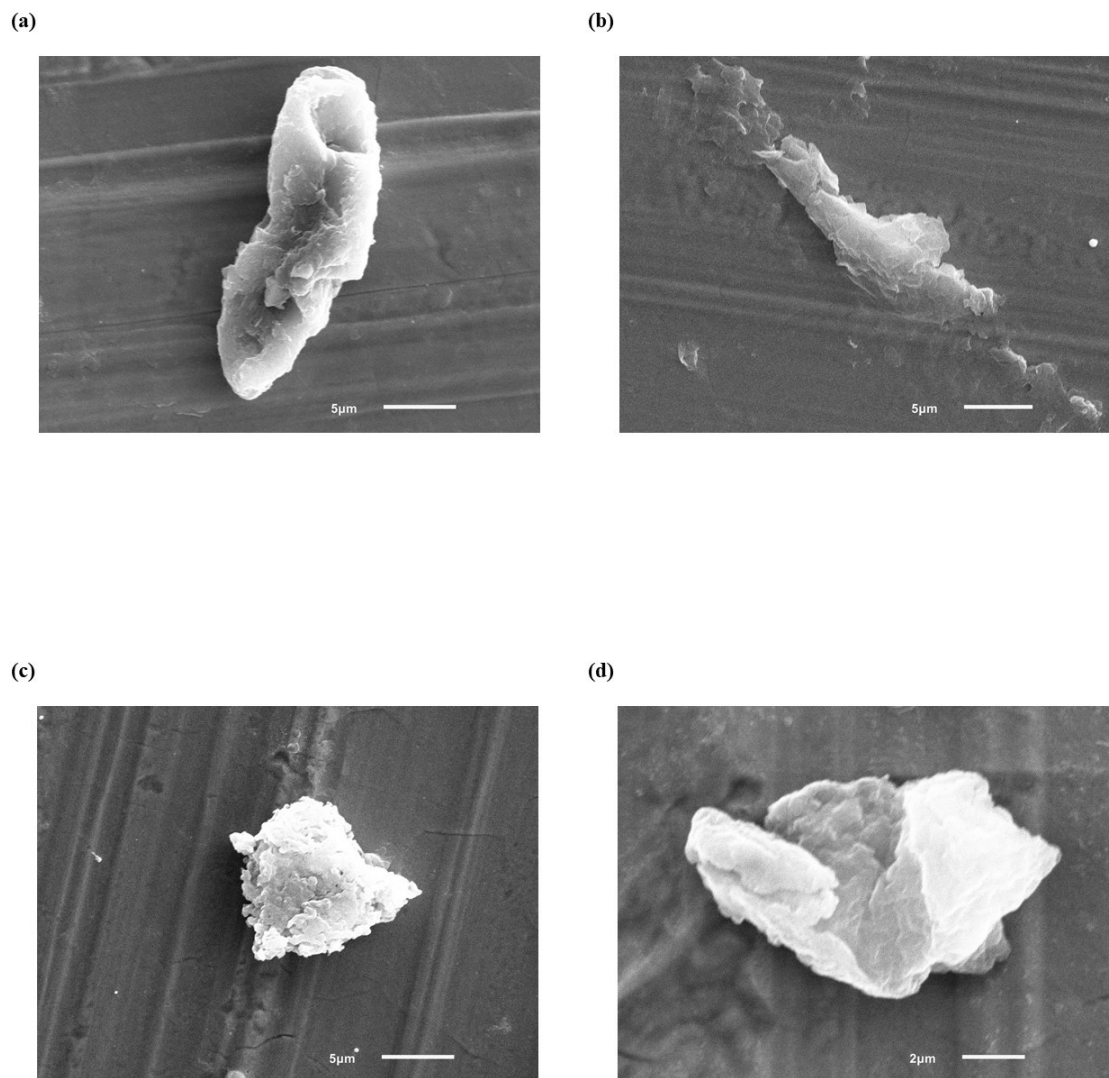


Figure C.1. SEM images of lead phosphate particles in presence of (a) 1 mM Ca^{2+} , (b) 3 mM Ca^{2+} , (c) 3 mM Ca^{2+} + 10 mg C/L PPHA, and (d) 3 mM Ca^{2+} + 10 mg C/L LHA.

