

## Introduction & Significance

- Lead exposure impacts the brain, kidneys, and cardiovascular system.<sup>1,2</sup>
- Lead found in the blood can be correlated with the concentration of lead in drinking water.<sup>1</sup>
- Orthophosphate is used to reduce lead at the consumer's tap by forming relatively insoluble divalent lead orthophosphate compounds on the surface of lead materials.
- Chloropyromorphite has been identified as one of the most stable lead mineral found in distribution systems.<sup>3</sup>
- Objective: Evaluate the impact of orthophosphate on lead mineralogy and solubility, and the physical properties associated with the lead particles.

## Approach

### Controlled Batch Tests:

- Dissolved inorganic carbon (DIC) was varied with sodium bicarbonate
- Orthophosphate was adjusted using sodium orthophosphate monobasic ( $\text{NaH}_2\text{PO}_4$ ). Lead stock solution (lead(II) chloride or lead(II) nitrate) added to prepared water & stirred for 20 minutes
- pH controlled using automatic titrator (0.6 M HCl, 0.6 M  $\text{HNO}_3$  & 0.6 M NaOH)
- Filtered through 0.2  $\mu\text{m}$  filter and 30 kDa membrane ultrafilter (~5-9 nm pore size)
- Compared experimental results to projections made in an existing model.



Image 1 – Photograph of titration apparatus used in experiments

### Analysis:

- Mineral composition: XRD, SEM & TEM
- Particle charge:  $\mu\text{mcm/Vs}$  (Malvern Nano – ZS90)
- Particle size: nm (Malvern Nano – ZS90)
- Lead concentration: ICP-AES and ICP-MS

## Results

### Mineral Composition:

- XRD**
- In the absence of orthophosphate, hydrocerussite [ $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ] formed.
  - Hydroxypyromorphite [ $\text{Pb}_5(\text{PO}_4)_3(\text{OH})$ ] formed in the chloride-free conditions and the additional presence of pyromorphite [ $\text{Pb}_5(\text{PO}_4)_3(\text{Cl})$ ] could not be totally ruled out when chloride was present.

### SEM/TEM

- Crystal structures were consistent with hydrocerussite and pyromorphites (Figure 1 and 2).
- Conditions where insufficient amounts of orthophosphate to completely precipitate with lead were present, a mix of (hydroxy)pyromorphite and hydrocerussite were present (Figure 1).

### Charge:

- (Hydroxy)Pyromorphite particles were considerably more negatively charged (-1.09 to -3.819  $\mu\text{mcm/Vs}$ ) than hydrocerussite particles (-0.125 to -3.906  $\mu\text{mcm/Vs}$ ) and charge became more negative as pH increased (Figure 5). Charge was relatively not impacted by orthophosphate dose.

## Results

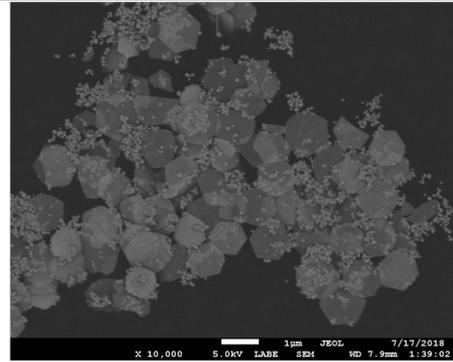


Figure 1 – SEM image of a hydrocerussite/(hydroxy)pyromorphite mix.

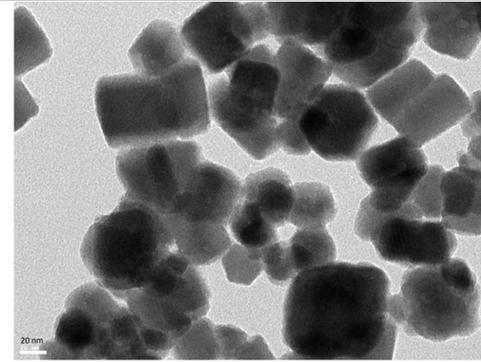


Figure 2 – TEM image of small (hydroxy)pyromorphite particles.

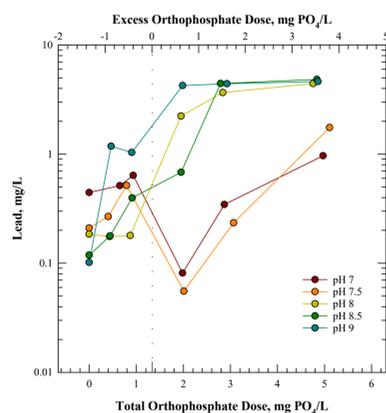


Figure 3 – Measured lead passing through a 0.2 micron filter for DIC of 10 mg C/L. The dashed line represents the stoichiometric equivalent of  $\text{PO}_4$  to precipitate lead.

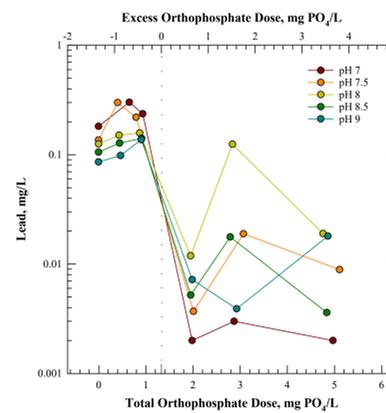


Figure 4 – Measured lead passing through a 30 kDa ultrafilter for DIC of 10 mg C/L. This was the criteria used to determine solubility. The dashed line represents the stoichiometric equivalent of  $\text{PO}_4$  to precipitate lead.

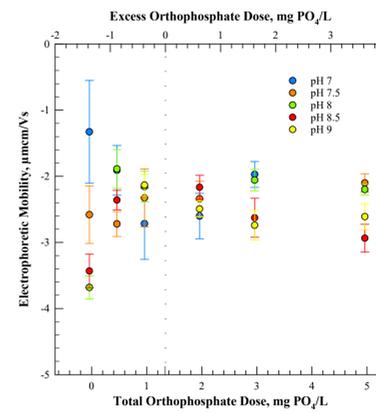


Figure 5 – Particle charge for all conditions with DIC of 50 mg C/L. The dashed line represents the stoichiometric equivalent of  $\text{PO}_4$  to precipitate lead.

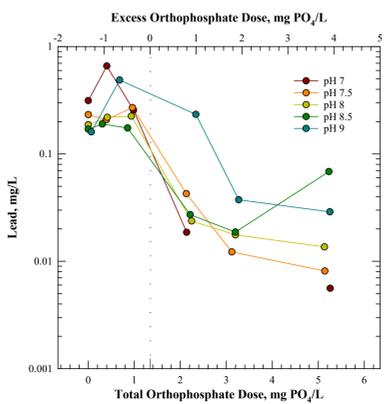


Figure 6 – Measured solubility for conditions with DIC of 50 mg C/L. The dashed line represents the stoichiometric equivalent of  $\text{PO}_4$  to precipitate lead.

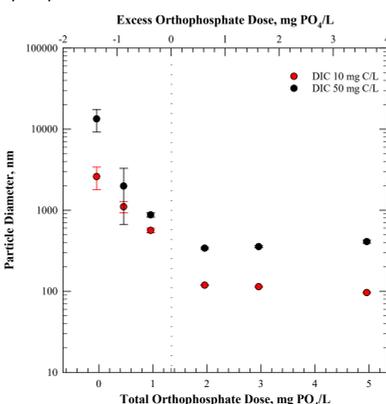


Figure 7 – Size comparison of samples with DIC 10 and 50 mg C/L. The dashed line represents the stoichiometric equivalent of  $\text{PO}_4$  to precipitate lead.

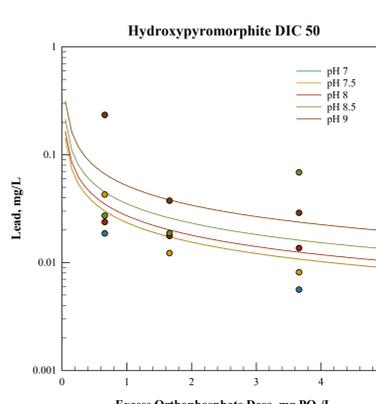


Figure 8 – Modeled solubility for hydroxypyromorphite plotted with experimental solubility results. ( $\text{Log}K = -66.77$ )<sup>4</sup>.

Note: "Excess" orthophosphate dose refers to the soluble orthophosphate level in equilibrium with the solid phase (particles) or concentration of orthophosphate beyond the amount to meet the stoichiometric equivalent necessary to precipitate the lead. "Total" orthophosphate includes soluble and particulate-bound orthophosphate. Conditions where excess orthophosphate levels were < 0 produced mixed hydrocerussite/(hydroxy)pyromorphite suspensions (Figure 1).

## Results (Cont.)

### Size:

- (Hydroxy)pyromorphite particles were very small based on filtrations, SEM/TEM analysis, and size measurements. 0.2  $\mu\text{m}$  filtration failed to capture (hydroxy)pyromorphite particles and it was possible that a fraction of particles could pass ultrafiltration, particularly in DIC 10 mg C/L water (Figures 3 and 4).
- Particle size tended to decrease with increasing pH and orthophosphate concentration (Figure 7).
- Particles in higher DIC water were larger than lower DIC water (Figure 7).
- (Hydroxy)pyromorphite particles ranged in size between 20 nm to 90 nm, and 60 nm to 200 nm in DIC 10 mg C/L and 50 mg C/L, respectively.

### Lead Concentration/Solubility:

- The addition of orthophosphate (in excess) greatly reduced the solubility of lead (II) at all pH values (Figure 6).
- In DIC 10 mg C/L water, the impact of pH and orthophosphate on the solubility of lead was not clear (Figure 4) and may be because some particles could pass ultrafiltration.
- In DIC 50 mg C/L water, solubility of lead (II) generally decreased with increasing pH and orthophosphate concentration in agreement with hydroxypyromorphite theoretical solubility predictions using -66.77 as the log K value<sup>4</sup> (Figure 8).
- Lead ranged 0.085 mg/L to 0.313 mg/L for hydrocerussite, 0.098 mg/L to 0.658 mg/L for mixed solids, and 0.003 mg/L to 0.233 mg/L for (hydroxy)pyromorphite.

## Conclusions

- Orthophosphate greatly decreased the solubility of lead (II) as (Hydroxy)pyromorphite is formed. Because the properties of hydroxypyromorphite and pyromorphite are nearly identical, and chloride was in the system, additional analyses are necessary to verify particle identity. Experiments are also being repeated in the absence of chloride.
- Measured lead levels fit theoretical lead solubility model predictions for hydroxypyromorphite reasonably well.
- (Hydroxy)pyromorphite particles were very small and easily pass a 0.20  $\mu\text{m}$  filter. Particles in lower DIC water were smaller than when formed in higher DIC water and a fraction could pass the ultrafilter. This could explain solubility data variability and model fit differences.
- (Hydroxy)pyromorphite particles were considerably more negatively charged than hydrocerussite particles.

## Collaborators

- Contributors: Jacob Botkins, Christy Muhlen, David Wahman

## References

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- 2-Lanphear B.P, Rauch S, Auinger P, Allen R.W, and Hornung R.W. (2018). *Lancet Public Health* **3(4)**: 177-184.
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