



## Effects of natural organic matter on calcium and phosphorus co-precipitation



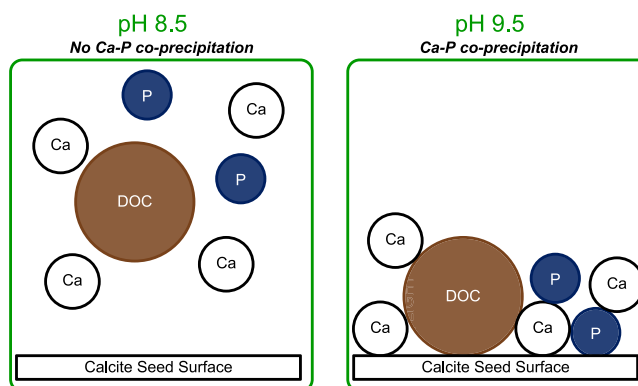
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### HIGHLIGHTS

- Dissolved organic carbon inhibits calcium and phosphorus co-precipitation.
- Dissolved organic carbon and phosphorus can co-precipitate with calcium at high pH.
- Aromatic dissolved organic carbon preferentially inhibits calcium precipitation.
- Phosphorus density on calcite is higher with increased dissolved organic carbon.
- High pH sites promote phosphorus co-precipitation with calcite in natural systems.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Phosphorus (P), calcium (Ca) and natural organic matter (NOM) naturally occur in all aquatic ecosystems. However, excessive P loads can cause eutrophic or hyper-eutrophic conditions in these waters. As a result, P regulation is important for these impaired aquatic systems, and Ca–P co-precipitation is a vital mechanism of natural P removal in many alkaline systems, such as the Florida Everglades. The interaction of P, Ca, and NOM is also an important factor in lime softening and corrosion control, both critical processes of drinking water treatment. Determining the role of NOM in Ca–P co-precipitation is important for identifying mechanisms that may limit P removal in both natural and engineered systems. The main goal of this research is to assess the role of NOM in inhibiting Ca and P co-precipitation by: (1) measuring how Ca, NOM, and P concentrations affect NOM's potential inhibition of co-precipitation; (2) determining the effect of pH; and (3) evaluating the precipitated solids. Results showed that Ca–P co-precipitation occurs at pH 9.5 in the presence of high natural organic matter (NOM) ( $\approx 30 \text{ mg L}^{-1}$ ). The supersaturation of calcite overcomes the inhibitory effect of NOM seen at lower pH values. Higher initial P concentrations lead to both higher P precipitation rates and densities of P on the calcite surface. The maximum surface density of co-precipitated P on the precipitated calcite surface increases with increasing NOM levels, suggesting that NOM does prevent the co-precipitation of Ca and P.

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## 1. Introduction

Phosphorus (P), calcium (Ca) and natural organic matter (NOM) play an important role in both surface waters and drinking water treatment systems. P, Ca, and NOM (measured as dissolved organic carbon (DOC)) naturally occur in every aquatic ecosystem; however, excessive P loads can cause eutrophic or hyper-eutrophic conditions in surface waters. These conditions are characterized by excessive primary productivity, reduction or depletion of dissolved oxygen, stressed aquatic organisms, and simplified trophic structure. P regulation is critical for many aquatic systems, and P co-precipitation with Ca, referred to as Ca–P co-precipitation in this study, is an important mechanism of natural P removal. Studies have shown, however, that DOC concentrations as low as 2.5 mg C L<sup>-1</sup> can inhibit Ca precipitation and significantly reduce calcite (CaCO<sub>3</sub>) growth (Hoch et al., 2000; Lin et al., 2005). Thus, DOC may negatively affect removal of P in natural systems by inhibiting Ca–P co-precipitation, but more research is necessary to assess the extent of this effect. Determining the role of DOC in Ca–P co-precipitation is important for identifying mechanisms that may limit P removal in natural and engineered systems where high P levels are a concern.

The interaction of P, Ca, and DOC is also relevant for water treatment and distribution systems. P is often introduced during water treatment processes for corrosion control and enhancement of biofiltration processes (Lauderdale et al., 2012). Ca is introduced during water treatment for lime softening, and DOC is a natural component of the raw water. The interactions of P, Ca, and DOC have significant implications for the effectiveness of corrosion control processes, biofiltration, and lime softening.

P and DOC both compete for active crystal growth sites with the free calcium ion, Ca<sup>2+</sup>, leading to lower calcite precipitation rates, which has the potential to hinder the softening process (Lin et al., 2005; Lin and Singer, 2006). P is also used for nutrient enrichment of biofiltration process that remove DOC (Lauderdale et al., 2012). As a result, the potential interactions of P, Ca, and DOC will be important for this emerging technology.

Corrosion studies have pointed to complex reactions between P, Ca, and DOC. The potential interactions of P with Ca and DOC can cause both positive and negative effects on corrosion control. For example, the formation of apatites (a group of calcium phosphorus minerals) can reduce corrosion in copper distribution systems; however, phosphate use in copper pipes can also decrease the formation of a protective malachite layer (Dartmann et al., 2004). DOC in the water may affect the performance of scale formation by decreasing the formation of Ca–P complexes, which may or may not be beneficial to corrosion control depending on the inhibitor used, the DOC concentration, and the material in the distribution system. An improved understanding of how P, Ca, and DOC interact will help water treatment professionals design and operate systems with better efficiency and reduced corrosion.

Previous work on P, Ca, and DOC has focused solely on the interactions between two of these three constituents. Studies have evaluated DOC and Ca, and their results show that DOC can significantly inhibit Ca precipitation in natural and engineered systems (Hoch et al., 2000; Lin et al., 2005). Other studies have looked at the importance of Ca–P co-precipitation to P removal in natural waters. Diaz et al. (1994) showed large decreases in aqueous P concentrations in response to pH and calcium increases. However, to the authors' knowledge, no work has been completed on all three of these water chemistry parameters at the same time. Simultaneous evaluation of P, Ca, and DOC is needed to determine how DOC affects Ca–P co-precipitation, thus enabling a better understanding of P removal by precipitation in both engineered and natural systems.

The main goal of this research is to assess the role of DOC in Ca and P co-precipitation. The specific objectives are to: (1) measure how the DOC concentration affects Ca–P co-precipitation, (2) compare the effect of differing pH values on Ca–P co-precipitation in the presence of DOC, (3) determine the types of minerals precipitated, and (4) evaluate whether DOC co-precipitates with either Ca or P during calcite precipitation.

## 2. Materials and methods

### 2.1. pH-stat apparatus

A pH-stat system was used to study the effect of DOC and P concentration on Ca–P co-precipitation rates. Tomson and Nancollas (1978) introduced the pH-stat system, which creates a constant degree of supersaturation relative to a solid phase by maintaining solution pH and composition. All experiments were conducted in a 600 mL jacketed beaker (Ace Glass, Inc.) The jacket contained circulating water from a temperature controlled water bath that insured all experiments were conducted at 25 °C. For this study, Acros Organics 99+% ACS reagent calcite seed crystals (CaCO<sub>3</sub>), purchased from Fisher Scientific (Cat. No. AC423511000), were introduced as a dry-powder into an experimental solution (see Section 2.2) with equimolar Ca and CO<sub>3</sub> concentrations, which caused the precipitation of calcite and decreased the solution pH. The specific surface area of the calcite seed was 0.323 m<sup>2</sup> g<sup>-1</sup> as determined by a six-point N<sub>2</sub>-BET method (Brunauer et al., 1938). The experimental solutions were stirred at a rate sufficient for good mixing. Equal volumes of 0.053 M (I = 0.1 M) CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> titrant solutions were added using a syringe pump (Harvard Apparatus 22) to return the pH to the set value (either 8.5 or 9.5), and maintain the constant degree of supersaturation. These titrant solutions were based on concentrations in previous research used to estimate calcium precipitation in the presence of NOM (Hoch et al., 2000; Lin et al., 2005). The titrant solutions are not the same as the experimental solutions (see Section 2.2), which were added to the jacketed beaker before the addition of the calcite seed. The syringe pump was controlled using a PHCN-37 pH controller (Omega Engineering) with a Thermo Fisher Orion 9156BNWP electrode to maintain solution pH. The pH controller maintained pH within ±0.05 pH units of the set value. The pH controller was calibrated daily with pH 7 and 10 standards (Fisher Scientific). A datalogger (CR510, Campbell Scientific) was used to continuously record pH, time, and titrant volume added.

The amount of titrant used to maintain solution pH and the mass of added calcite seeds were used to calculate the amount of solid precipitated based on the following equation (Hoch et al., 2000; Lin et al., 2005):

$$\text{Ca Precipitation Rate} = \frac{S \times m}{G \times SA} \quad (1)$$

where  $S$  is slope (L s<sup>-1</sup>);  $m$  is the molarity of the titrant solution (μmol L<sup>-1</sup>);  $G$  is the mass of the calcite seed (g);  $SA$  is the surface area of the calcite seed (m<sup>2</sup> g<sup>-1</sup>); and Ca precipitation rates is in the units of μmol s<sup>-1</sup> m<sup>-2</sup>. Ca precipitation rates can be compared across experiments to determine the effect of different DOC and P concentrations on calcite precipitation.

### 2.2. Experimental solutions

Table 1 shows the composition of all reactor experimental solutions used in this study. A range of experimental times were used to allow the calculation of a single Ca and P precipitation rate (see Fig. 1) for each experiment shown in Table 1. The Ca precipitation

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