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# Mechanisms of Phosphorus Control in Urban Streams Receiving Sewage Effluent

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**Abstract** Urban streams often are a major source of phosphorus (P) to rivers, primarily due to large inputs of sewage effluent. A good example of this is Chicago (Illinois, USA) area streams, which make up most of the flow of the upper Illinois River. Even though streams in this section of the Mississippi River basin are characteristic hard-water systems and exhibit high calcium and carbonate concentrations, the precipitation of Ca–P minerals is minimal and phosphate is not removed from the water column. The objective of this study was to determine the chemical mechanisms controlling P activity in Chicago area streams. Measurement of dissolved ion activities on filtered surface water samples demonstrated that an average of 79% of P in the study streams was dissolved and the remaining was particulate (<0.05 µm and >1.0 µm in diameter, respectively). Neither a P colloidal-size fraction nor a correlation between dissolved and particulate Fe and P was observed. Thermodynamic modeling and SEM-EDS analysis of particulate matter in filter residues indicated that dissolved P may adsorb and co-precipitate on the surface of calcite rather than precipitating in a pure Ca–P mineral phase. Although SEM-EDS results also suggested that P was adsorbed to silicate minerals, organic residues likely dominated the P-containing particulate fraction. Sediment extraction results indicated that organic P was one of two major P components in the stream bottom. The Fe-associated P fraction represented the largest sediment-P fraction, and with little association between Fe and P in the overlying water, dissolved inorganic P may have aided in the authigenic formation of an Fe–P sediment phase. Overall, results suggest that pH combined with Ca and Mg activity are the dominant chemical controls on P chemistry in this P enriched system.

**Keywords** Phosphorus · Streams · Urban · Sewage effluent · Water quality · Sediments

## 1 Introduction

The influence of N and P on both the eutrophication of local streams (Dodds et al. 2002; Dodds and Welch 2000) and the annual formation of a large hypoxic zone in the Gulf of Mexico (Rabalais et al. 2001) have been the impetus for numerous nutrient studies of rivers in the Mississippi River drainage basin.

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Agriculture is the major source of N and P to streams and rivers in this basin (Royer et al. 2006); however, a number of rivers are heavily impacted by P derived from sewage effluent point sources and carry large loads of P downstream. For example, an estimated 70% of P in the Illinois River and ~5% of the P load to the Gulf of Mexico comes from sewage discharged from Water Reclamation Plants (WRPs) in the Chicago area, which include some of the largest plants in the world (David and Gentry 2000).

Phosphorus in sewage effluent is predominantly in the dissolved form, but its in-stream concentrations can be controlled by a number of chemical processes. Many natural water systems are supersaturated with respect to hydroxyapatite and undersaturated with regard to more soluble Ca–P minerals (tricalcium phosphate, octacalcium phosphate, dicalcium phosphate dihydrate). Although hydroxyapatite precipitation in hard, alkaline water systems has yet to be thoroughly investigated, one study suggested that Ca–P minerals may nucleate only when the saturation index (SI) of hydroxyapatite >9.4 (SI-tricalcium phosphate >2.2); where

$$\mathrm{SI} = -\log\left(\frac{\mathrm{IAP}}{K_{\mathrm{sp}}}\right), \qquad (1)$$

and IAP and $K_{\mathrm{sp}}$ are the ion activity product and solubility product constant of the mineral species (Diaz et al. 1994). Thus, high concentrations of dissolved Ca and P, as well as alkaline pH, are characteristic of aquatic systems in equilibrium with Ca–P minerals (Moutin et al. 1992). Furthermore, the precipitation and dissolution of calcite in highly alkaline aquatic environments can be accompanied by P co-precipitation. Because dissolved P concentrations >0.61 mg P $L^{-1}$ inhibit calcite nucleation and poison crystal growth, the co-precipitation process will control aqueous P geochemistry only if dissolved P concentrations are initially low to moderate (House et al. 1986).

A number of fluvial systems with lower $PO_4^{3-}$ activities have shown equilibrium or association with a Fe–OH–$PO_4$ colloid of varying composition (Fox 1989). However, Fe–OH–$PO_4$ colloids with ratios Fe/P~2 have been reported for some aquatic systems with dissolved P concentrations >0.10 mg P $L^{-1}$ (Gschwend and Reynolds 1987; Lienemann et al. 1999; Gunnars et al. 2002). Although techniques for measuring colloidal Fe and P concentrations can have operational difficulties, conservative estimates can be made by carefully using sequential filtration. Because previous studies reported Fe–P colloids with diameters between 0.05–1.0 μm, Mayer and Jarrell (1995) used sequential vacuum filtration through polycarbonate membrane filters to separate the colloidal and particulate fractions and found that streams from the Tualitin Bay basin (Oregon) contained significant concentrations of colloidal Fe and P. They also found a strong, significant correlation ($R^2$=0.88) between Fe and P in the colloidal fraction, but not between Fe and P particulate concentrations.

The present study was conducted in an effort to understand the high solubility of P in Chicago area streams, which leads to large fluxes downstream. Because of the importance of downstream transport of P to the Gulf of Mexico (Sylvan et al. 2006), we need to fully understand controls on dissolved P in these and other urban streams receiving sewage effluent. We hypothesized that in-stream P concentrations were controlled by (1) equilibrium with an Fe–OH–$PO_4$ colloidal phase, or (2) dissolution–precipitation equilibrium with meta-stable Ca–P minerals. Phosphorus concentrations were measured throughout the year and were analyzed in comparison to other in-stream analytes on four low-flow occasions. Thermodynamic modeling and P composition analysis of suspended particulate matter and stream sediments were used to determine the dominant mechanisms of P control.

## 2 Materials and Methods

### 2.1 Study Background

Three streams from the Des Plaines and Chicago River watersheds (3,730 and 1,610 km$^2$, respectively) were sampled for this study: Des Plaines River—two sampling sites 18 km apart (Ogden Ave. and Irving Park Rd.); Salt Creek—two sampling sites 23 km apart (Wolf Rd. and JFK Blvd.); and one sampling site on the North Branch of the Chicago River (Fullerton Ave.; Fig. 1, Table 1). The Des Plaines and Chicago River watersheds were used for intensive sampling because they are highly urbanized and WRP effluent makes up a significant component of stream discharge. The study sites were concurrently used by the Metropolitan Water Reclamation District of

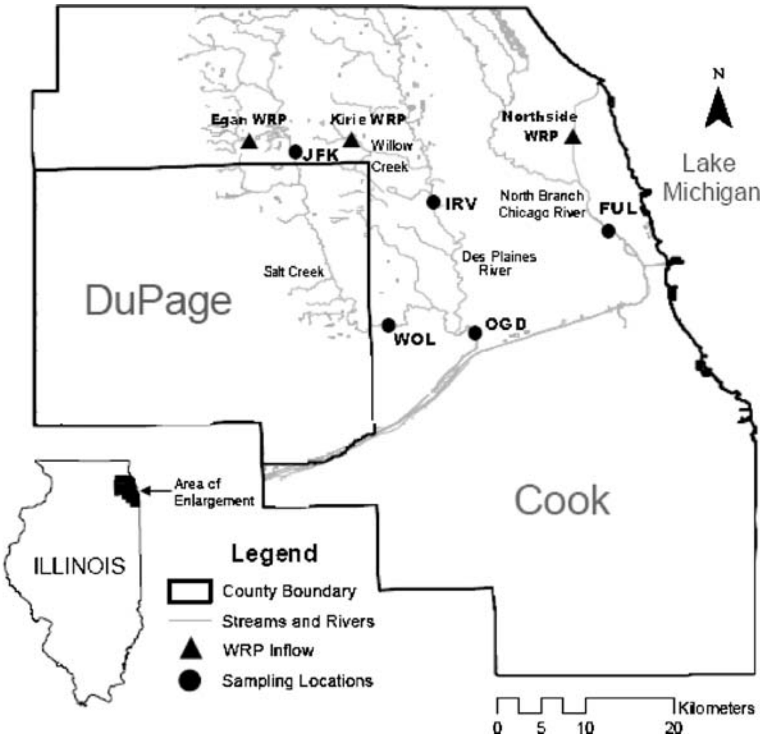

**Fig. 1** Map detailing the location of rivers, sampling sites, and large WRPs. Sampling site abbreviations are listed in Table 1

Greater Chicago (MWRDGC; Chicago, IL) for an intensive study of the linkages between stream dissolved oxygen dynamics (as controlled by algal production) and nutrient concentrations, utilizing representative streams receiving WRP inputs. Thus, samples and measurements taken at the sampling sites were meant to supplement long-term nutrient monitoring data.

**Table 1** Description of sampling site locations

| Sampling site | Abbreviation on map | River or stream | Lat/Long coordinates |
|---|---|---|---|
| Fullerton Ave. | FUL | N. Branch of the Chicago River | 41°55′30″ N<br>87°40′30″ W |
| Irving Park Ave. | IRV | Des Plaines River | 41°57′11″ N<br>87°51′14″ W |
| Ogden Ave. | OGD | Des Plaines River | 41°49′15″ N<br>87°48′39″ W |
| JFK Blvd. | JFK | Salt Creek | 42°00′19″ N<br>87°59′43″ W |
| Wolf Rd. | WOL | Salt Creek | 41°49′33″ N<br>87°54′00″ W |

Mean annual precipitation in the Des Plaines and Chicago River Watersheds is between 85 and 95 cm per year. Seasonal flooding of area streams occurs between March and May due to spring storms and snow melt. In addition to dolomitic bedrock composition, predominantly clayey-till quaternary deposits, and industrial and WRP effluent, other influences on stream chemistry are anthropogenic and include deicing salts, lawn fertilizers, and street dust (Chung and Finno 1992; Arnold et al. 1999; Groschen et al. 2004). Most importantly, water reclamation plants are a significant source of discharge and nutrients to the streams. The Egan, Kirie, and North Side WRPs are located in the study catchments, and are among the largest WRPs in the Chicago metropolitan region (effluent discharge=$89\times10^3$, $96\times10^3$, and $886\times10^3$ $\mathrm{m}^3$ $\mathrm{day}^{-1}$, respectively). Other studies have enumerated the point sources discharging effluent directly into Salt Creek, including six other WRPs between the JFK Blvd. and Wolf Rd. sampling sites and numerous industrial discharges (IEPA 2004). The JFK Blvd. sampling site is different from the others because it is located directly downstream from Busse Lake dam and the Egan WRP inflow. The Salt Creek at JFK Blvd. has also received stream bank stabilization and repair.

### 2.2 Sampling and Laboratory Procedures for Water Samples

Two sample collections from 2006 were analyzed for this study—the first was collected by the MWRDGC and the second set we collected for more intensive measurements. On each occasion, pH, temperature, and dissolved oxygen were measured on site.

The Metropolitan Water Reclamation District of Greater Chicago sampled the study streams on a monthly basis and more often during large rain events throughout 2006. In addition to on-site chemical parameters, unfiltered water samples were analyzed for total P (EPA method 365.4) and turbidity; and dissolved reactive P (DRP), $NH_4^+$, and $NO_3^-$ were measured after filtering the sample through a 0.45 μm membrane in the laboratory (EPA methods 365.1, 350.1, and 353.2, respectively; U.S. Environmental Protection Agency 2007).

We sampled the study streams on four low flow occasions in 2006 (August 30 or 31, September 18, September 26, and December 11), taking a 2 L sample each time. Dissolved oxygen, conductivity, and salinity were also measured on site. The water sample was sequentially filtered on site through 1.0 μm and 0.05 μm polycarbonate filters to obtain particulate (>1 μm), colloidal (0.05–1.0 μm), and dissolved (μm) concentrations of P and Fe. The colloid fraction was operationally defined on the basis that most Fe-(oxyhydr)oxide colloids are between 0.05 and 1.0 μm in diameter (Mayer and Jarrell 1995). Aliquots of filtered and unfiltered samples were acid preserved ($pH<2$) and kept on ice while in the field. Our lab regularly filters water samples for dissolved P through 0.45 μm membrane filters upon returning to the lab, which is considered the standard pore size for water quality work. In order to compare dissolved P concentrations from the normal routine to that fractioned by sequential filtration at the sampling sites, another aliquot of non-acidified bulk sample was filtered through a 0.45 μm glass fiber filters after returning to the lab.

Dissolved P concentrations in filtered aliquots were measured using an automated ascorbic acid colorimetric method (Murphy and Riley 1962) on a Lachat QuikChem 8000 Flow Injection Analysis System (Hach Company, Loveland, CO). Total P was measured on acid-preserved unfiltered water samples using the ascorbic acid method after digesting solutions with ammonium persulfate and sulfuric acid (detection limit=0.7 μg P $L^{-1}$). Flame-atomized atomic absorption spectroscopy was used to measure Fe concentrations in unfiltered and 1.0 μm filtered water samples (detection limit=0.06 mg Fe $L^{-1}$). Total dissolved Fe was measured on 0.05 μm filtered samples using the ferrozine colorimetric method (Stookey 1970; detection limit=0.014 mg Fe $L^{-1}$).

Other dissolved analytes were also measured in filtered water samples: Na and K by atomic emissions spectroscopy; Mg and Ca by atomic absorbance spectroscopy; $NO_3^-$, $SO_4^{2-}$, and $Cl^-$ by ion chromatography; and $NH_4^+$ and $SiO_2$ by the salicylate and heteropoly blue methods, respectively. Calcium carbonate alkalinity was estimated by charge balance between the major cations and anions measured in the water samples (Stumm and Morgan 1996). We used internally and externally prepared QCs and randomly spiked samples to ensure high quality in our chemical measurements.

A JOEL JSM-6060LV low vacuum scanning electron microscope (SEM) with secondary and backscattered electron detectors and an ISIS energy dispersive X-ray spectroscopy (EDS) system was used to analyze residue on sequential extraction filters from the September 18, 2006, sampling. Images and spectra were taken from carbon-coated filters. Backscattered electron images of filter residue were adjusted to maximize image contrast in order to find particles composed of elements with higher atomic masses. Numerous particles from each filter were analyzed for elemental composition using EDS. The sample size of P-containing particulates ranged from 1 to 6 because of the difficulty in finding such particles in the filter material.

### 2.3 Sampling and Laboratory Procedures for Sediment

Sediment from the Des Plaines River and Salt Creek sites was sampled on September 18 and 26, 2006. A representative fraction of soft sediment was sampled by pressing a plastic cup (6.3 cm in diameter and 7 cm deep) into sediment from the center of the stream multiple times. Sediment was sieved through a 4 mm mesh to eliminate coarse materials, and to allow the sequential extraction to be as representative as possible of the bulk material. The sediment samples were kept on ice in an amber 500 mL bottle until we arrived at the laboratory. Sediment samples were then transferred to Whirl-Pak™ bags, frozen, freeze–dried, and stored in the dark at 4°C.

Subsamples of freeze-dried sediments were ground to a fine powder and extracted in triplicate for various P phases using the extractants and washings described in the SEDEX method (Ruttenberg 1992). To summarize, a 0.10 g sample of sediment was extracted for lightly adsorbed P with 1 M $MgCl_2$; Fe-associated P with a citrate-dithionite-bicarbonate (CDB) solution; P in Ca-mineral and co-precipitated in calcite with a pH 4 acetate buffer; and organic and recalcitrant P phases by ashing at 550°C. Phosphorus concentrations in extract solutions were determined colorimetrically using the ascorbic acid method and matrix matching. One exception was that Fe-associated P was first separated from the CDB matrix by co-precipitation with $Mg(OH)_2$ and then measured colorimetrically after acid dissolution (Huerta-Diaz et al. 2005).

### 2.4 Thermodynamic Modeling and Data Analysis

Analyte concentrations and pH data were used to assess the activity of various phosphate species in each sample. A matrix based approach was used to solve equilibrium constants and obtain solution activity values (Giambalvo 1996). Complexation constants for the major anions and cations were taken from Stumm and Morgan (1996) and the model adjusted their values with regard to ionic strength using the Davies equation.

Saturation indices for calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and the dominant Ca–P minerals were calculated for each sample using appropriate activities given by the thermodynamic model. Solubility product constants for the mineral species were from Stumm and Morgan (1996) (HAP, hydroxyapatite—$Ca_5(PO_4)_3OH$; DCPD, dicalcium phosphate dihydrate—$Ca(HPO_4)_2.H_2O$; and TCP, amorphous tricalcium phosphate—$Ca_3(PO_4)_2$), Gregory et al. (1974) (OCP, octacalcium phosphate–$Ca_4H(PO_4)_3$), Plummer and Busenberg (1982) (calcite), and Nordstrom et al. (1990) (dolomite). All statistical methods were performed in MS Excel 2003. Average concentrations or compositions are reported herein as average±SE. All statistical tests used a 0.05 significance level.

## 3 Results and Discussion

### 3.1 Stream Water Chemical Parameters and Modeling

The four supplementary samples showed that the Chicago area study streams were primarily alkaline and had high concentrations of dissolved cations and anions (Table 2). Sodium and Cl concentrations were high most likely because of sewage effluent from WRPs using Cl as a disinfectant and from NaCl-rich de-icing salts in street dust (Terrio 1994; Talmage et al. 1999). Calcium, Mg, and $HCO_3^-$ concentrations were also high, which reflects the influence of dolomitic derived surface soils and bed rock geology on surface water quality. The overall average of $NO_3^-$ and $NH_4^+$ concentrations measured in the study streams on a monthly basis (5.3±0.2 and 0.20±0.02 mg N $L^{-1}$, respectively) were not significantly different from those measured in the four supplementary samples (5.7±0.4 and 0.25±0.08 mg N $L^{-1}$, respectively; *P*-values>0.29).

Unlike most agriculture drainage streams in Illinois (Figueroa-Nieves et al. 2006), P concentrations in the Chicago area streams were much greater than $NO_3^-$ concentrations. Monthly total P concentrations measured in the Chicago area streams during 2006 were persistently high and showed seasonal variation (Fig. 2). Low total and dissolved P concentrations were measured between fall and spring, and P concentrations often increased greatly during the period of low summer discharge. Concentrations of total P in the four intensive samples corresponded well with the monthly samples. A significant rain event between the monthly and sub-sample taken in December was probably responsible for the difference in total P concentrations. Overall, total P and DRP concentrations measured in the four samples were not significantly different from the annual average concentrations from each site (*P*-values>0.23). Given that average total P, DRP, pH, $NO_3^-$, and $NH_4^+$ concentrations at each site were not significantly different between the two sets of samples, the four supplementary samples were assumed to be good representations of average stream conditions.

Phosphorus concentrations in the 1.0 and 0.05 μm filtered aliquots at each site were not significantly different (*P*-values>0.27, except Fullerton Ave where *P*-value=0.08), suggesting that the P-colloid fraction was negligible. Hydrolysis of the P-containing partic-

**Table 2** Mean values for chemical measurements and P concentrations from the supplementary sampling of the Chicago streams

| Measure | North Branch of the Chicago River | Des Plaines River | | Salt Creek | |
|---|---|---|---|---|---|
| | Fullerton Ave. | Irving Park Rd. | Ogden Ave. | JFK Blvd. | Wolf Rd. |
| pH | 7.4 (0.1) | 7.8 (0.1) | 7.7 (0.1) | 7.8 (0.1) | 7.8 (0.1) |
| Temp (°C) | 18.3 (3.4) | 16.0 (4.4) | 17.8 (3.2) | 15.1 (4.6) | 16.9 (3.7) |
| DO (% Saturation) | 83.8 (1.5) | 89.9 (2.2) | 90.7 (1.1) | 89.1 (3.8) | 87.7 (2.7) |
| $\kappa°$ (μS) | 660 (76) | 840 (100) | 760 (80) | 810 (110) | 800 (69) |
| Ca (mg Ca $L^{-1}$) | 61.5 (4.8) | 74.3 (12) | 60.0 (5.5) | 60.5 (10) | 67.6 (10) |
| Na (mg Na $L^{-1}$) | 89.3 (14) | 112.3 (2.1) | 124.5 (11) | 98.1 (14) | 126.7 (14) |
| Mg (mg Mg $L^{-1}$) | 21.5 (2.9) | 29.8 (6.9) | 22.0 (3.2) | 25.7 (4.5) | 25.1 (4.5) |
| K (mg K $L^{-1}$) | 7.6 (0.6) | 8.5 (0.6) | 8.5 (0.5) | 7.5 (0.4) | 8.3 (0.5) |
| $Cl^-$ (mg Cl $L^{-1}$) | 113 (17) | 158 (8) | 160 (16) | 149 (12) | 155 (18) |
| $SO_4^{2-}$ (mg S $L^{-1}$) | 17.2 (2.0) | 25.0 (2.9) | 23.0 (2.7) | 23.6 (3.2) | 26.0 (3.9) |
| $NO_3^-$ (mg N $L^{-1}$) | 5.9 (0.9) | 4.3 (0.6) | 7.5 (0.8) | 4.7 (0.6) | 6.3 (0.9) |
| Alk (mg $CaCO_3$ $L^{-1}$) | 212 (22) | 233 (19) | 196 (15) | 179 (32) | 236 (24) |
| $SiO_2$ (mg Si $L^{-1}$) | 5.9 (0.5) | 7.4 (0.9) | 7.0 (0.8) | 5.5 (0.3) | 6.3 (0.3) |
| DOC (mg C $L^{-1}$) | 5.2 (0.4) | 7.6 (0.1) | 6.8 (0.3) | 6.9 (0.3) | 6.7 (0.2) |
| Total Fe (mg $L^{-1}$) | 0.41 (0.08) | 1.23 (0.34) | 0.99 (0.23) | 0.52 (0.09) | 0.74 (0.15) |
| 1.0 μm Fe (mg $L^{-1}$) | 0.16 (0.02) | 0.29 (0.05) | 0.20 (0.03) | 0.25 (0.02) | 0.25 (0.03) |
| 0.05 μm Fe (mg $L^{-1}$) | 0.03 (0.03) | 0.03 (0.01) | 0.04 (0.03) | 0.06 (0.03) | 0.04 (0.01) |
| Total P (mg $L^{-1}$) | 1.0 (0.1) | 0.73 (0.06) | 2.2 (0.4) | 0.88 (0.06) | 1.5 (0.3) |
| 1.0 μm P (mg $L^{-1}$) | 0.79 (0.08) | 0.52 (0.04) | 2.0 (0.5) | 0.61 (0.06) | 1.33 (0.04)[a] |
| 0.05 μm P (mg $L^{-1}$) | 0.77 (0.08) | 0.54 (0.02) | 2.02 (0.5) | 0.65 (0.08) | 1.34 (0.01)[a] |
| DRP (mg P $L^{-1}$) | 0.83 (0.08) | 0.54 (0.04) | 2.0 (0.5) | 0.64 (0.05) | 1.3 (0.3) |

Standard errors are reported in parentheses ($n$=4 and [a] $n$=3)

DO Dissolved oxygen, $\kappa°$ specific conductivity (referenced to $T$=25°C), *alk* alkalinity, *DOC* dissolved organic carbon, *DRP* dissolved reactive phosphorus

ulate matter was minimal, as suggested by the insignificant difference between DRP concentrations and P concentrations in the 1.0 and 0.05 μm filtered samples ($P$-values>0.19). Dissolved reactive P concentrations were strongly correlated with total P in both the intensive samples and the monthly samples taken outside of precipitation events ($r^2$=0.997 for $n$= 20 and 0.932 for $n$=89). Ratios of DRP to total P for these samples were 0.75±0.01 ($n$=20) and 0.79±0.02 ($n$=89). Other studies reported relatively high DRP/total $P$ values from streams impacted by WRP effluent, but not as large as those found in the Chicago area study streams (Van der Perk et al. 2006). The DRP/total P values reported here imply that WRP effluent inflows are a constant source of dissolved P to the study streams throughout the entire year.

In contrast to P concentrations in the study streams, a significant Fe colloidal fraction was present. The Chicago area streams contained on average 0.78± 0.11 mg Fe $L^{-1}$, 95±1% of which was found in the particulate and colloidal size fractions. Besides a slightly significant correlation between dissolved Fe and total P concentrations ($r$=0.57 and $P$-value< 0.025), no significant co-variation was observed among the Fe and P fractions (total, particulate, colloidal, and dissolved). The high Fe and P concentrations in the Chicago area streams are similar to those measured in river systems that have shown dissolved P control by Fe-colloids (Mayer and Jarrell 1995; Fox 1989). In contrast to these other studies, however, the Chicago streams also have high concentrations of Ca, Mg, Na, Cl, and $HCO_3^-$, which can affect the speciation of both Fe and P. The diffuse boundary layer of Fe-hydroxide colloids can be suppressed in the presence of high concentrations of dissolved cations and anions, thereby decreasing the tendency for $PO_4^{3-}$ ions to migrate and adhere to the colloid surface (Stumm and Morgan 1996). Also, cations and anions can flood the surfaces of minerals and colloids, working to exchange adsorbed phosphate through mass transfer.

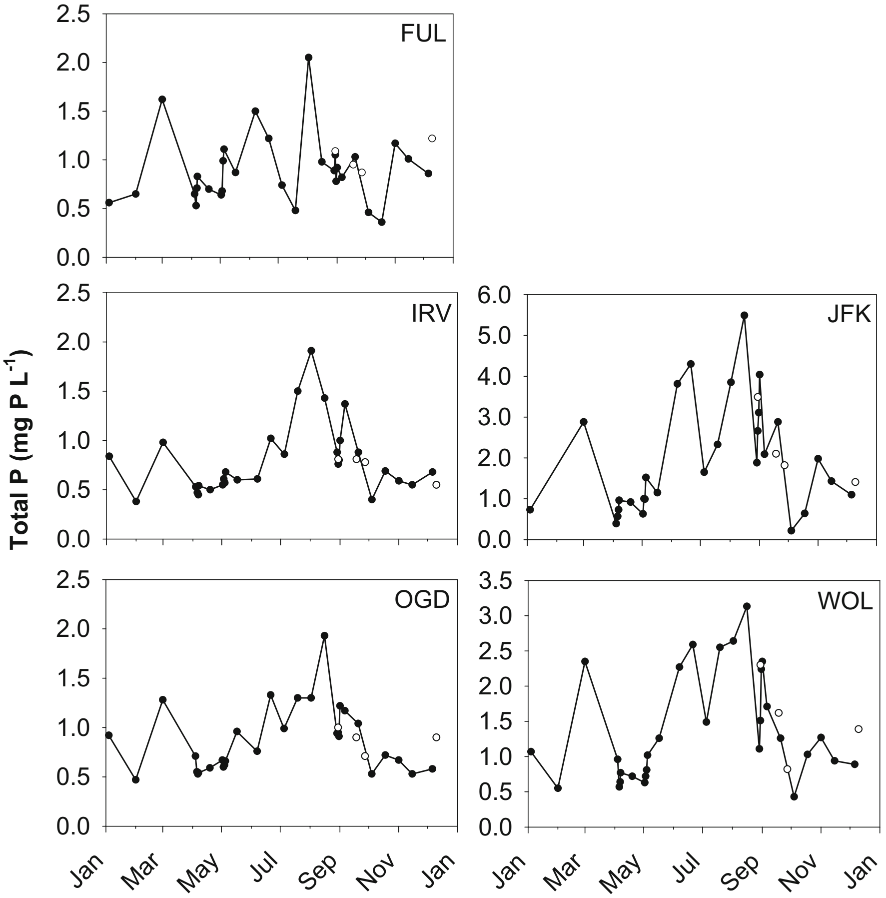

**Fig. 2** Total P concentrations measured in the Chicago streams during 2006. *Closed dots* represent P measured by MWRDGC, and *open dots* represent total P concentrations of supplementary samples collected for intensive analysis. Note different scales

Phosphate speciation for the Chicago area stream water samples indicated that dissolved P concentrations were dominated by Mg and Ca complexes with $HPO_4^{2-}$ (Fig. 3). Because much of the dissolved P present in the Chicago streams was sequestered by dissolved cations, $PO_4^{3-}$ activity, the predominantly mineral active species, was relatively low. Of the meta-stable mineral species, DCPD was

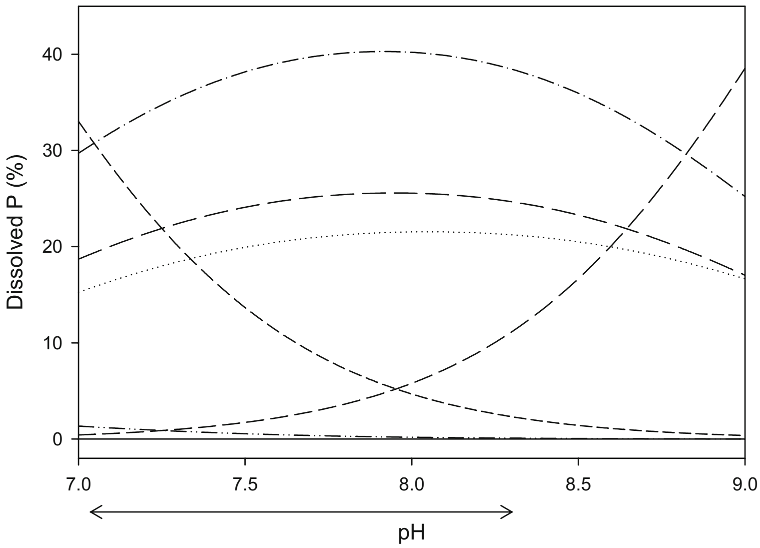

**Fig. 3** Simulated P speciation of a solution comparable to Chicago stream samples (1.5 mg P L$^{-1}$, 162 mg Ca (HCO$_3$)$_2$ L$^{-1}$, 146 mg Mg (HCO$_3$)$_2$ L$^{-1}$, and 246 mg NaCl L$^{-1}$). The *arrow* represents the range of pHs measured in the study streams during 2006.
Key: ———— $PO_4^{3-}$,
·············· $HPO_4^{2-}$,
– – – – – $H_2PO_4^{1-}$,
– ·· – ·· – ·· – $CaH_2PO_4^{1-}$,
—— —— —— $CaHPO_4^{0}$,
– · – · – · – $MgHPO_4^{0}$,
— — — $CaPO_4^{1-}$

nearest saturated levels ($SI_{DCPD}=-1.54\pm0.05$), while OCP and TCP were much more undersaturated ($SI_{OCP}=-2.8\pm0.2$, $SI_{TCP}=-3.8\pm0.1$). Hydroxyapatite, however, was significantly over-saturated ($SI_{HAP}=5.8\pm0.2$) at the four supplementary sampling times, but precipitation of HAP may be just as unlikely as the meta-stable Ca–P minerals. Reports have suggested that hydroxyapatite nucleation in natural water systems may not occur until $SI_{HAP}>9.4$ due to kinetic inhibition, and that more soluble mineral species will likely precipitate prior to hydroxyapatite (Diaz et al. 1994; Plant and House 2002). In hard water systems saturated with calcite an increase in pH will raise $PO_4^{3-}$ activity, and HAP or meta-stable Ca–P minerals may precipitate (House 1999). In the presence of high concentrations of Mg, $PO_4^{3-}$ is sequestered into dissolved complexes and the more soluble Ca–P phases may remain undersaturated (Fig. 4). As a result, large changes in the pH of the Chicago streams may not result in the precipitation of Ca–P minerals. Presuming that DRP, Ca, and Mg concentrations remain consistent, it is reasonable to expect Ca–P mineral equilibrium to have a minimal effect on decreasing P solubility during average stream conditions throughout the year.

Calcite and dolomite activity were near equilibrium during the supplementary sampling period, which was expected given the bedrock geology. Furthermore, $H_3PO_4$ potential showed close correlation with the variance of $CaCO_3$ and $CaMg(CO_3)_2$ activity about their solubility products (for $-\text{Log } CaCO_3$ and $-\text{Log } CaMg(CO_3)_2$ vs $-\text{Log } H_3PO_4$, $r=-0.926$ and 0.922, respectively; P-values<0.001). These results coincide with other reports that have suggested that P concentrations in hard water rivers may fluctuate because P co-precipitates on calcite (Avnimelech 1980; Salingar et al. 1993). However, calcite precipitation rates can be significantly reduced by the presence of dissolved P, and mineral nucleation and growth can be completely inhibited by concentrations of dissolved P>0.62 mg P $L^{-1}$ (House et al. 1986). Because P concentrations were high in the Chicago area streams, calcite precipitation is probably inhibited or reduced throughout much of the year, and it is unlikely that calcite or dolomite precipitation cleanses P from the water column as found in hard-water lakes.

## 3.2 Sediment Extraction

Sediment texture among the sampling sites, while not directly measured, consisted of gravel and sand at JFK Blvd., and contained considerably less gravel and more silt and clay size material at Wolf Rd., Ogden Ave., and Irving Park Ave. Total P concentrations in sediment from Salt Creek and Des Plaines River were high (JFK Blvd.=1,900±550; Wolf Rd.=3,300±290; Irving Park Rd.=2,600±210; Ogden Ave.=1,700±340 mg P $kg^{-1}$), primarily resulting from large concentrations of Fe-associated and organic P (Fig. 5). While chemical parameters from the water

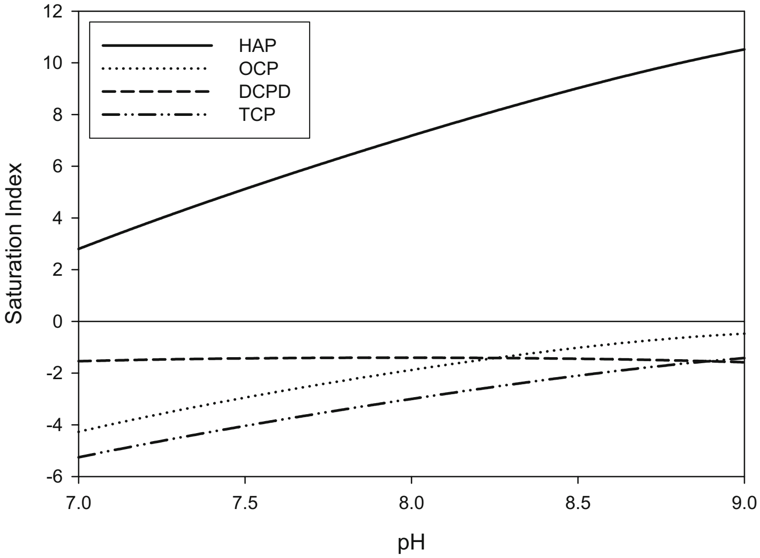

**Fig. 4** Saturation indices for a simulated solution comparable to average conditions in the Chicago streams (1.5 mg P $L^{-1}$, 162 mg $Ca(HCO_3)_2$ $L^{-1}$, 146 mg $Mg(HCO_3)_2$ $L^{-1}$, and 246 mg NaCl $L^{-1}$)

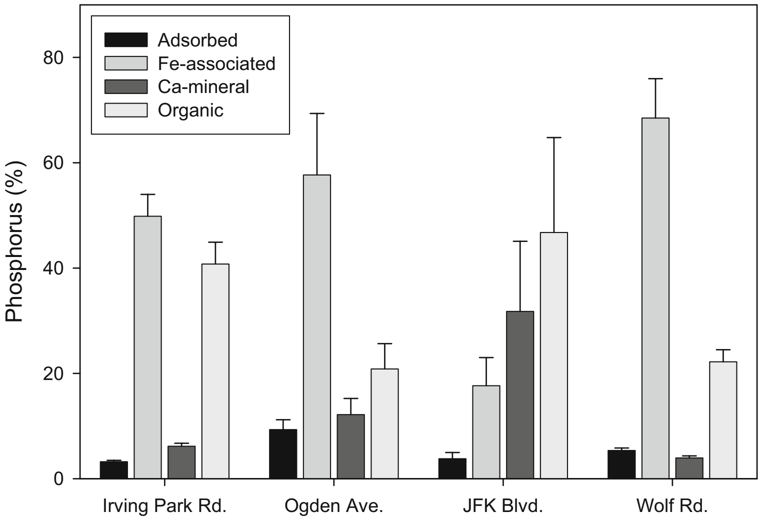

**Fig. 5** Sediment P fractionation in samples from Chicago streams, with each fraction presented as percent of sediment total P concentration. *Error bars* represent SE ($n=2$)

samples suggest that the interaction between Fe and P in stream surface waters was negligible, the sediment environment was conducive to the formation of a measurable Fe–P phases. Subsurface P and $Fe^{2+}$ concentrations are high in deeper sediments because of an oxidized barrier at the sediment-water interphase. As a result, sediment conditions of the Des Plaines River and Salt Creek may be conducive to vivianite formation (House and Denison 2002; Taylor and Boult 2007); however, mineralogical data is needed to confirm the presence of $Fe^{2+}$–P compounds in the sediment subsurface. Phosphorus inputs from WRP's in the Chicago area also aide in the accumulation of organic P in stream sediments. In P-limited ecosystems organic P experiences fast and efficient turnover; yet the high dissolved P concentrations in the study streams easily support microbial metabolic activity. Thus, organic-P residues collect in stream sediments or are transported downstream.

The Ca–P mineral fraction–pure Ca–P minerals and calcite/dolomite co-precipitated P–represented one of the smallest pools of P extracted from the Chicago stream sediment samples, with the exception of sediment sampled at JFK Blvd. Phosphorus-containing $CaCO_3$ particulates were likely the main species extracted using the acetate buffer from the sediment samples because the chemical conditions of the overlying water did not promote the precipitation of HAP or other metastable Ca–P minerals. Low concentrations of Ca-associated P in the sediments are not surprising because high dissolved P concentrations inhibit nucleation and crystal growth of $CaCO_3$.

The extraction for lightly adsorbed P exchanged phosphate species bound in the outer-sphere of sediment substrates was done via mass transfer with high concentrations of $Cl^-$. Adsorption phenomena is not to be confused with specific inner-sphere phosphate-substrate interactions (precipitation, co-precipitation, etc.) that the other extraction steps measured. Much like P co-precipitation on $CaCO_3$, adsorption phenomena are self limiting. High dissolved P concentrations and low amounts of suitable substrate are probably responsible for the minimal contribution that adsorbed P made to total sediment P (<10% of total P among all sites). Even though adsorbed P concentrations were not high, dissolved P from the overlying water was responsible for the overall sediment composition of the Chicago streams; high dissolved P likely encouraged the formation of Fe–P phases and accumulation of organic P in sediments. Differences in the JFK Blvd. sediment samples from the general composition trend probably arose because of the heterogeneous sediment composition and greater total P concentrations in the overlying water at this site.

### 3.3 Analysis of Filter Residues

Use of SEM and EDS was originally intended to evaluate the composition of both colloidal and particulate material containing P. However, the results of this study suggest that P in the Chicago streams is found only in the particulate and dissolved fractions. As a result, the filter residue collected on 1 μm filters was assessed to determine the predominant forms of particulate P found in the study streams.

Particulate residue consisting primarily of heavier elements collected at the Chicago sites represented a small fraction of the material found on the filters (Fig. 6a). Amorphous organic matter, as determined by electron backscattering, was found in large clumps all over the filters. Elemental mapping of organic matter clumps did not show accumulations of P any greater than background levels (data not shown); however, the sheer magnitude of organic versus inorganic particulate residues on the filters and the high concentration of organic P in the sediments suggest that organic-P compounds were most likely the dominant form of P in particulate matter from the water column.

Matter from the particulate fraction that contained heavier elements and was analyzed for total percent composition using EDS. Of the numerous particles observed, most were composed of Si, Al, and Fe, and showed negligible amounts of P (<0.5%), which further suggest that the bulk of P-containing particulate matter is not inorganic, but is associated with organic residues. However, a small subset of particles analyzed yielded measurable P concentrations along with significant amounts of Si, Al, Fe, Ca, and Mg (Table 3). Sodium and Cl were also found, but in relatively small proportions compared to the other constituents. Elemental analysis of particulates in filter residue showed that two distinct types of P-containing particles were present. Residue matter composed of greater amounts Si, Al, and Fe, and lower percentages of Ca, Mg, and P, were found on filters from all sites (Fig. 6b; particles F-1, I-1, I-2, I-3, O-1, J-1, and W-1 through W-6). Particulates of this type were likely ferro-alumino-silicate minerals eroded from stream bank material or surface soils. The P content of the silicate minerals varied depending on the stream system, and ranged from 1.2 to 2.5% P (*w*/*w*) for the Des Plaines and Chicago Rivers, and from 6.1 to 34.2% P (*w*/*w*) in Salt Creek. Water samples from Salt Creek showed the highest dissolved P concentrations among all of the streams, which likely increased the amount of P adsorbed and occluded in particulate matter suspended in the water column.

A second type of P-containing particle found in filter residue from the Des Plaines River at Ogden Ave. was composed primarily of Ca and P (Fig. 6c; particles O-2, O-3, O-4). Overall, these particles were

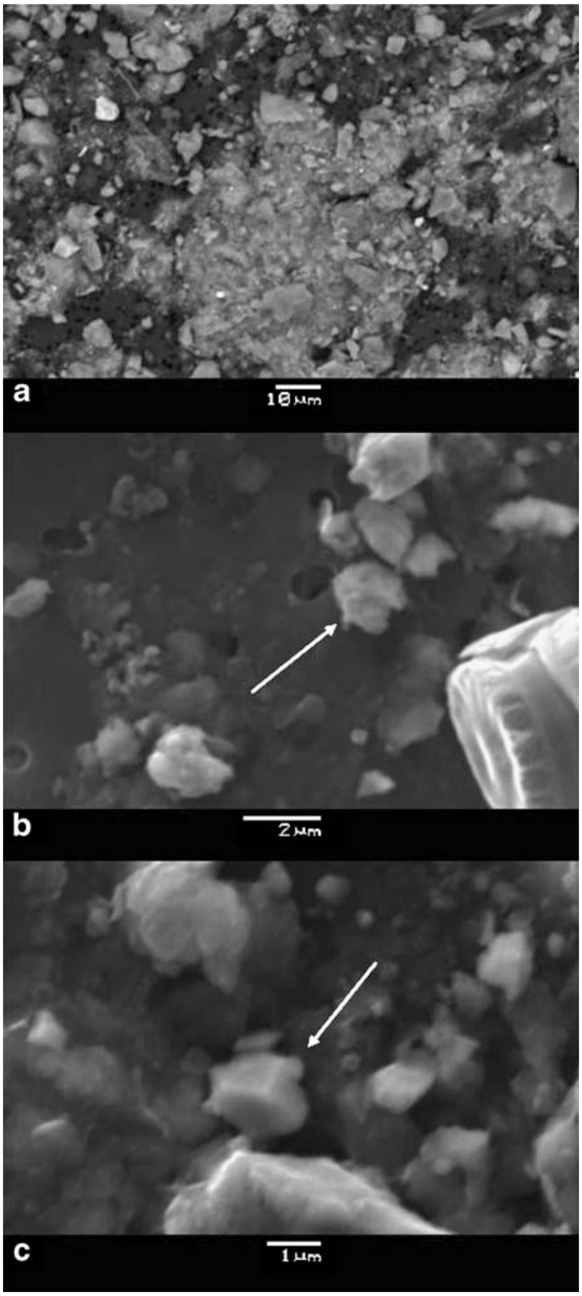

**Fig. 6** SEM images of filter residue. **a** Backscattered electron image of bulk material from the Des Plaines River at Irving Park. **b** Secondary electron image of J-1, a particle with low P and high Si, Fe, and Al composition in filter material from the Salt Creek at JFK Blvd. **c** Secondary electron image of particle O-4, which has high P and Ca composition in filter material from the Des Plaines River at Ogden Ave. (*arrows* mark the particle of interest)

**Table 3** Elemental composition of P-containing particulate matter in water sampled from Chicago streams on September 18, 2006

| Location | Reference number | Elemental composition (*w*/*w*) | | | | | |
|---|---|---|---|---|---|---|---|
| | | P | Al | Si | Fe | Ca | Mg |
| Fullerton Ave. | F-1 | 1.5 | 13.2 | 39.0 | 44.6 | 1.7 | |
| Irving Park Rd. | I-1 | 2.2 | 9.9 | 26.7 | 48.8 | 6.2 | 6.2 |
| | I-2 | 1.2 | 19.9 | 59.4 | 7.3 | 6.8 | 5.5 |
| | I-3 | 2.5 | 19.0 | 58.4 | 12.8 | 2.6 | 4.7 |
| Ogden Ave. | O-1 | 14.5 | 5.6 | 11.0 | 51.6 | 14.8 | 2.6 |
| | O-2 | 18.0 | 9.2 | 27.2 | | 43.3 | 2.3 |
| | O-3 | 22.2 | 4.5 | 10.1 | | 62.2 | 1.1 |
| | O-4 | 29.1 | | 3.1 | | 67.8 | |
| | O-5 | 11.6 | 36.9 | 51.5 | | | |
| | O-6 | 2.4 | 3.2 | 2.7 | 88.8 | 2.2 | 0.7 |
| JFK Blvd. | J-1 | 3.4 | 9.0 | 38.3 | 35.9 | 6.0 | 7.5 |
| Wolf Rd. | W-1 | 16.5 | 19.9 | 53.9 | 2.2 | 3.2 | 4.4 |
| | W-2 | 34.2 | 48.2 | 16.0 | | 1.6 | |
| | W-3 | 10.4 | 12.8 | 31.5 | 31.9 | 7.4 | 6.0 |
| | W-4 | 6.1 | 15.7 | 38.3 | 30.1 | 4.0 | 5.8 |
| | W-5 | 14.3 | 24.9 | 54.5 | | 2.2 | 4.1 |
| | W-6 | 17.4 | 15.3 | 32.2 | 18.0 | 8.2 | 9.0 |

Samples were collected on 1.0 μm filters and particulate compositions were analyzed using energy dispersive X-ray spectroscopy.

Ca-rich in comparison to pure Ca–P minerals (Ca–P minerals have P/Ca ratios >0.59; P/Ca ratio of 0.40± 0.02 from Ogden Ave. filter, $n=3$), suggesting that P was adsorbed or had been co-precipitated on $CaCO_3$. Likewise, an SEM image of one such particle showed rhombohedral geometry, a common feature of crystalline $CaCO_3$ (Fig. 6c). Particles with this composition were only found on the Ogden Ave. filter, which may imply that P co-precipitation on calcite is a site-specific occurrence or that a terrestrial source of calcite was present near the downstream sampling site on the Des Plaines River. However, more in-depth investigations are needed in order to fully determine the sources or formation of P-containing calcium carbonates in Chicago streams.

## 4 Conclusions

Sewage and industrial effluent in the Chicago area has led to high concentrations of dissolved anions and cations to the streams of the Upper Illinois River Basin. These naturally hard-water streams and rivers regularly experience ionic strengths greater than 10 mmol $L^{-1}$, greatly complicating in-stream geochemistry. Sequential filtration of water samples showed that dissolved P species represented on average 79% of total P and that colloidal P concentrations were negligible. Even though a significant fraction of total Fe was in the colloidal size fraction, P interactions with the Fe species were likely inhibited because of the activity of Ca, Mg, and $HCO_3^-$. Overall, slightly alkaline hydrogen activity and dissolved cations ($Ca^{2+}$, $Mg^{2+}$, and $Na^+$) exerted primary control on inorganic P speciation. As a result, $PO_4^{3-}$ activity was too low to induce spontaneous precipitation of HAP and meta-stable Ca–P minerals. Sediment extractions and SEM-EDS analysis confirmed that phosphate adsorption to suspended particulate matter and co-precipitation on the surface of calcite represent subsidiary controls on in-stream P concentrations, and likely do not reduce stream concentrations greatly. The overwhelming influence of Fe–P phases on sediment composition stands in contrast to observations that Fe-containing colloids and particulate matter in the water column were inhibited from sequestering significant concentrations inorganic P. The paucity of Fe–P species in the overlying water seems to suggest authigenic formation of these substances in the sediments. However, more research is needed into the mechanism of Fe–P deposition in stream sediments, especially with regard to the influence of high dissolved P from Chicago area point sources.

Although recent efforts have been made to set P standards for streams and rivers in the United States and the State of Illinois, the P concentrations of the Chicago area streams may be difficult to address.

Given the high solubility and limited removal mechanisms for dissolved P in the streams studied, P will continue to be transported downstream. To reduce this load, P will need to be removed from the effluent before discharge, as is done at many treatment plants throughout the US and world (Oleszkiewicz and Barnard 2006). In addition, more research is needed to assess the P phases in sediments from the Chicago streams, their specific interaction with P in the overlying water, and the need for P remediation of stream beds.

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