STRUVITE RECOVERY FROM SMALL WASTEWATER TREATMENT PLANTS

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Problem

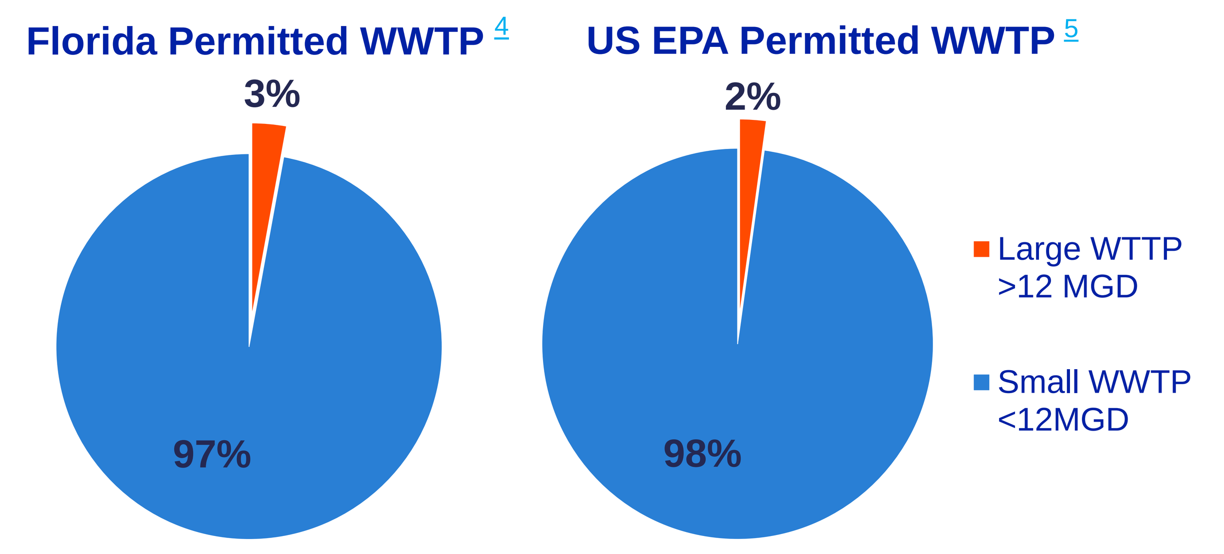
Global demand for phosphorus (P), a finite resource derived from phosphate rock (P_2O_5), is estimated at 40 million tons per year and is increasing by 1.5% annually[1]. An estimated 7 billion tons of P_2O_5 remain in reserves that can be economically mined but are expected to be exhausted within this century.[2] A sustainable source of P is essential to help feed the world's growing population.

Hypothesis

Struvite recovery from small, wastewater treatment plants (WWTPs) may provide an environmentally and economically sustainable alternative to fertilizer P.

Project Overview

- Municipal WWTP digestate may be a source of renewable fertilizer as $NH_4MgPO_4{\cdot}6H_2O$ (struvite).
- Most struvite applications target digestates from large WWTPs using anaerobic bioreactor technologies.
- However, approximately 97%–98% of state and nationally permitted WWTPs are small with discharges less than 12 million gallons per day (MGD).[3]



Study Locations

Four locations were selected to represent two of the three most common variations of wastewater treatment processses.[6] These locations treat wastewater solids (sludge) by the aerobic digestion process, which is a biochemical oxidative stabilization of wastewater sludge.

Table 1. Aerobic digestate chemical properties.

WWTP	pH	ORP	ALK ($CaCO_3$)	NH_4^+	PO_4^{3-}	Mg^{2+}	Ca^{2+}	Iron	Al^{3+}
		mV	-----------------mM L-1						-----------------
Gadsden East	7.69	2573	4.19	7.00	1.51	1.15	1.39	0.02	0.05
Killearn	7.96	225	12.48	28.42	4.58	0.87	1.15	0.02	0.03
Lake Jackson	7.72	271	3.47	6.21	1.29	0.73	1.02	0.01	0.03
Meadows	8.11	227	6.06	9.55	0.37	0.46	1.09	0.05	0.05

pH Effects on IAPs

Activities of Mg^{2+}, NH_4^+, PO_4^{3-} were calculated using Visual MINTEQ 3.1[7] and K_{sp}=13.26.[8] Ion Activity Products (IAPs) were calculated at digestate pH from 4.0 to 14. Precipitates were allowed in order to estimate the minimum pH at which struvite would form. Then, precipitates were not allowed in order to estimate the level of supersaturation attainable (Fig. 1).

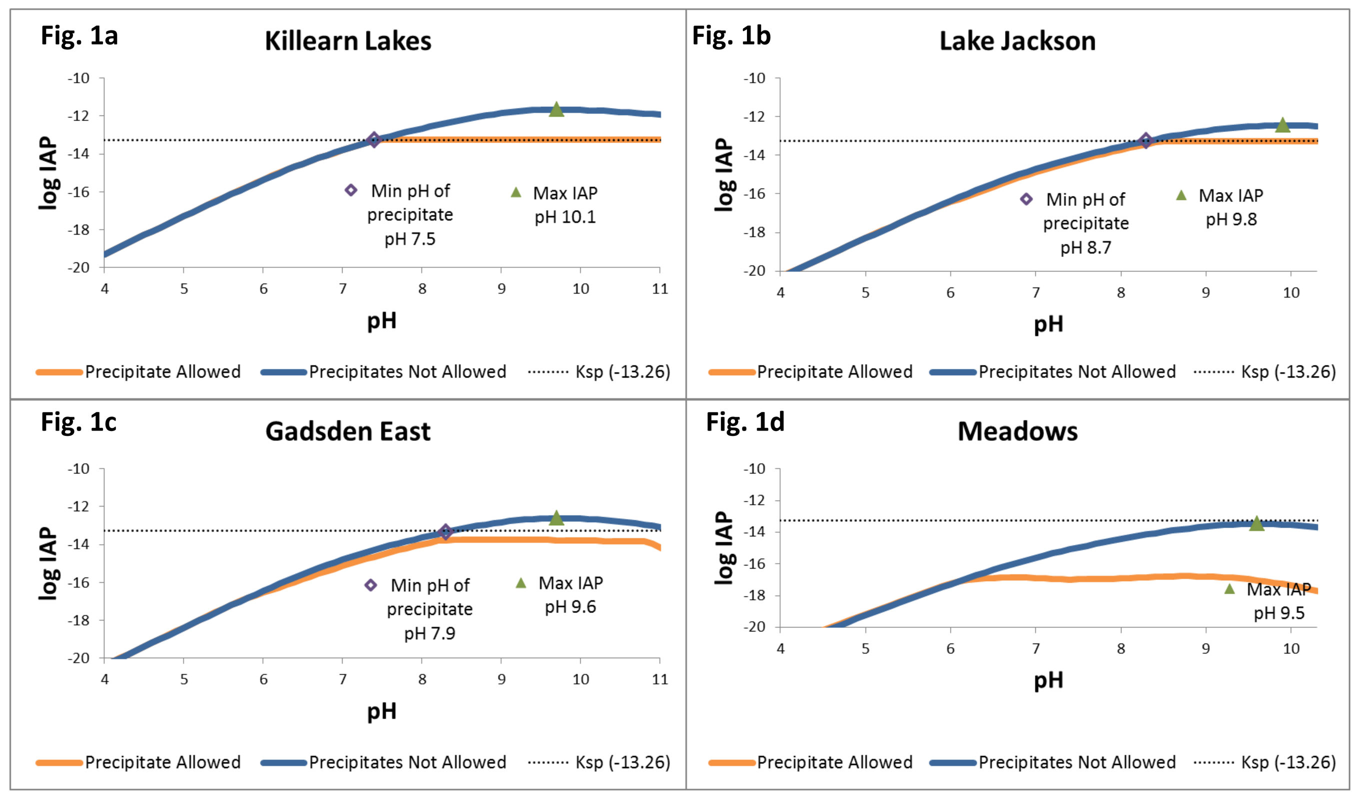


Fig. 1. Identifying the pH range for maximizing struvite formation in digestates from four WWTPs.

Competing Solid Phases

The Mg^{2+} and PO_4^{3-} ions react to form compounds other than struvite, especially in the presence of Ca^{2+}, particularly at high pH[9]. Struvite precipitation kinetics was shown to be two times faster than amorphous calcium phosphate (ACP) and an order of magnitude faster than magnesite and newberyite[10,11]. The MINTEQ-IAP is not a kinetics model, but it can be configured to exclude the formation of slow-precipitating species. Under simulation conditions, brushite ($CaHPO_4\ 2H_2O(s)$) was the most likely struvite competitor (Fig. 2).

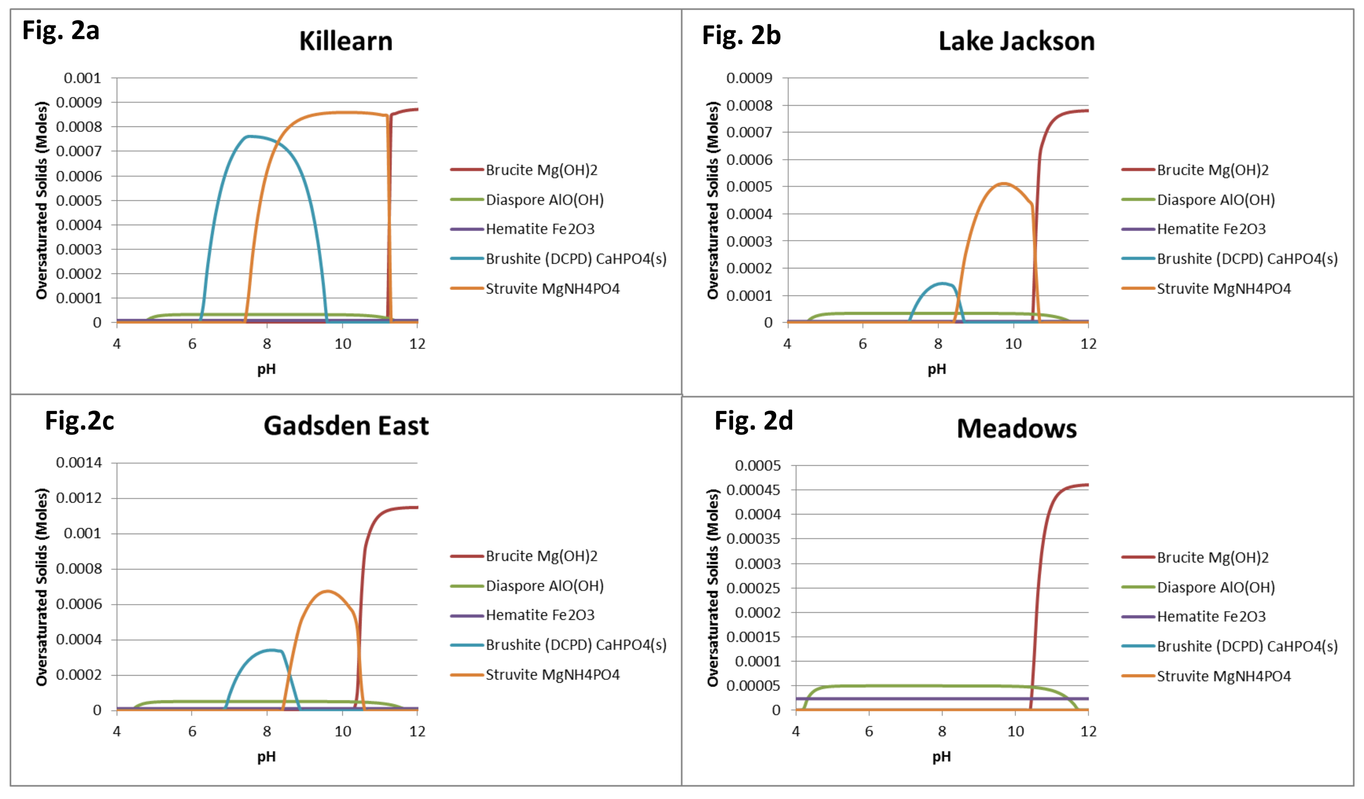


Fig. 2. Potential formation products in digestates from four WWTPs.

Struvite Formation

A pH range from 8.0 to 10.7 was estimated for maximizing struvite formation from anaerobic WWTPs.[12] However, it was reported that high struvite production, in terms of P removal, can be achieved at a pH of ~7.5 with >80% efficiencies.[13]

Near neutral conditions might lessen calcium-based precipitates[7] and other coprecipitates from competing for Mg^{2+} and PO_4^{3-} ions. Using the data from the oversaturated solids and values in Table 1, the pH 8.8 was selected to determine the P removal efficiency and the kilogram of P produced per year. (Table 2).

Table 2. Estimated recovery from lower pH digestates.

WWTP*	Minimum struvite solubility		Struvite (pH 8.8)	Struvite P Recovery from digestate (pH 8.8)
	mM	pH	mM	%
Gadsden East	0.676	9.6	0.428	45
Killearn	0.512	9.7	0.825	18
Lake Jackson	0.860	10.1	0.297	26

**Meadows location was subject to significant infiltration and inflow, which diluted the digestate species activities below what is required for significant struvite formation.*

A laboratory experiment was conducted to test the effect of solution pH on struvite formation by simulating the inorganic chemistry found at the WWTPs. Struvite concentration can be calculated based on $[NH_4^+]$, if the hydraulic residence time (HRT) and pH are known (Eq. 1).[14]

$$Struvite\ [^{mol}/_{L}] = [NH_4^+]_{Precipitated} = [NH_4^+]_{Intial} - [NH_4^+]_{Final} \quad \text{(Eq. 1)}$$

Solution NH_4-N was measured initially (T_0) and at 24 hours (T_{24}) to estimate solid formation. The percent struvite yield was calculated using Eq. 2. The theoretical yield was calculated from the MINTEQ-IAP model and the observed yield was calculated from $[NH_4^+]_{final}$

$$\%\ yield = \frac{actual\ yield}{theoretical\ yield}\ x\ 100 \qquad \text{(Eq. 2)}$$

Eq. 2 resulted in a 70.6% struvite yield. The molar concentration of $NH_{3(g)}$ was not factored into the observed yield as it did not significantly affect the struvite yield, according to the model. The formation experiment was then carried out under similar conditions using Killearn digestate (Table 3).

Table 3. Struvite recovery from Killearn digestate.

WWTP	MINTEQ IAP model Struvite		Measured Struvite Precipitation		Yield
	mM	pH	mM	pH	%
Killearn	0.105	8.5	0.85	8.5	81

Conclusions

- The Visual MINTEQ model supports struvite recovery from small WWTPs under neutral to moderately alkaline conditions.
- The next step is to better identify and quantify solid phase products and study increasing P recovery through increasing Mg:P ratio.
- Finally move to pilot-scale production of struvite at select WWTP to determine observe struvite production rates.

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