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STRUVITE (MgNH₄PO₄· 6H₂O) SOLUBILITY AND ITS APPLICATION TO A PIGGERY EFFLUENT PROBLEM

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ABSTRACT

Struvite ($MgNH_4PO_4\cdot 6H_2O$) solution chemistry was studied in order to understand a struvite scaling problem which exists in the pipe network of a series of 4 effluent lagoons at a piggery. Struvite deposits frequently occur in piping from the final effluent pond intended for irrigation purposes, causing severe scaling of the pipe, making irrigation or other end uses of the effluent impossible. The conditional solubility constant ($P_s = S_{Mg}\cdot S_{NH_3-N}\cdot S_{PO_4-P}$, equilibrium S values (M)) was determined over the range of pH values (6.8-8.5) and solution concentrations of Mg, NH_3-N and PO_4-P close to field conditions, and at a temperature of $30^\circ C$. A comparison of field and laboratory data indicates struvite precipitates from the second lagoon onwards. The solubility data obtained also indicate potential for precipitation as a method of nutrient removal from wastewaters.

KEYWORDS

struvite; magnesium-ammonium-phosphate; solubility; precipitation; nutrient removal; wastewater; piggery; effluent.

NOMENCLATURE

In this paper, the following nomenclature is used :
S_X = the soluble concentration of the material X.
P_s = the Conditional Solubility Constant, defined as -

$$P_s = S_{Mg}\cdot S_{NH_3-N}\cdot S_{PO_4-P}$$

the S values are for equilibrium within the system (units are M).
Q_s = the Provisional Solubility Product, defined as for P_s, with the difference being it is the S value product at any time and is not necessarily an equilibrium product.
σ_X = the standard deviation (*n-1*) of the quantity X
bar over item (e.g. $\overline{S_{Mg}}$) = mean of that measurement

INTRODUCTION

A piggery (with approximately 20 000 animals) near Mandurah, Western Australia uses a series of 4 effluent lagoons (Mean hydraulic residence time = 30 days) to treat the waste produced. When wastewater from the final lagoon was diverted (via piping) for irrigation, crystallization identified by X-ray diffraction analysis as struvite ($MgNH_4PO_4\cdot 6H_2O$) and residual organic material, occurred in the piping and after a few weeks the scaling was so severe that piping the effluent had to cease. Similar problems have been reported in a number of municipal and agricultural waste treatment systems (Borgerding (1972); Roberto Jnr. and Sweeten (1985); Snoeyink and Jenkins (1980); Westerman *et al.* (1985)). Severe precipitation of struvite from piggery effluents is to be expected, as a result of the high concentrations of ammoniacal nitrogen and phosphorus from the breakdown of organics, and magnesium included as a feed supplement and in groundwater

used to carry waste to the lagoon system. There appears to have been little quantification of the scaling problem in piggeries. A first step would be a determination of the solubility of struvite under conditions of the effluent disposal lagoons. Understanding of the struvite solution chemistry would also enable an assessment of the potential for the recovery of struvite from the effluent to be made, since struvite is a valuable slow release fertilizer (Liberti *et al.* (1983)), Rothbaum and Rohde (1976)).

The solubility product (as pK_{sp}) and the conditions used are summarized in Table 1. Existing solubility data are somewhat disparate, and the experimental conditions used are quite different for each determination. The solubility product (as pK_{sp}) and the conditions used are summarized in Table 1.

TABLE 1 - pK_{sp} determinations and the conditions used

Mean pK_{sp}	T(°C)	Solution Conditions	Reference
12.6	38	Saturated urine samples	Elliot *et al* 1959
12.33	38	$0.015 < I < 0.02$, Pure saturated solutions	Johnson 1959
13.15	25	$I < 0.05$, Pure components	Taylor *et al* 1963
12.6	25	Total solute concentration $< 0.01M$	Bube 1964
13.12	25		
12.97	35		
12.94	38	Saturated solution of solid	Burns and Finlayson 1982
12.84	45		

These measurements have been made principally to aid in the understanding of the etiology of struvite formation as kidney and urinary stones in humans and other mammals. This is a serious pathological condition.

The calculated behaviour of struvite at varying pH values in solution has also been reported and expressed in various forms (Snoeyink and Jenkins (1980); Stumm and Morgan (1981); Verplaetse *et al.* (1985,1986)).

The aim of the work reported in this paper was to determine at what point in the lagoon system struvite precipitation was likely to occur, by experimentally measuring the solubility of struvite under conditions close to the wastewater in the lagoons.

MATERIALS AND METHODS

The experimental programme consisted of the measurement of effluent parameters in the piggery, followed by laboratory determination of the solubility of struvite under conditions close to those in the lagoons.

Field Measurements

Conditions existing in the lagoon system relevant to struvite deposition were determined by a 24 hour sampling study. Samples for analysis were taken every 4 hours, while pH and temperature measurements were made every 2 hours over the duration of the study (11-12 April 1988). Samples were filtered through Whatman GF/C type glass fibre filters, diluted and acidified with concentrated H_2SO_4 to pH of approximately 3. S_{Mg} was determined by atomic absorption spectrophotometry, S_{NH_3-N} and S_{PO_4-P} measurements were made using spectrophotometric methods, following Standard Methods (APHA (1985)). pH and temperature measurements were made using a battery powered portable pH meter.

Laboratory determinations of P$_s$

Analytical Reagent (A.R.) grade chemicals were used for all solution preparations and analyses. A set of 250mL conical (or Erlenmeyer) flasks were used as the reaction vessels and were sealed with plastic film (Parafilm). Approximately 1g of borosilicate glass grindings were placed in each sample as nucleation sites. Temperature regulation was achieved by containing the samples in an agitating water bath at $30^\circ C$. pH adjustment was made using a solution of 0.4M NaOH. Filtering of samples was achieved by membrane filtration ($0.45\mu m$ pore size) after glass fibre (GF/C) filtration. Sample solutions were weighed out and diluted into separate ranges for the individual analyses. S_{Mg}, S_{NH_3-N} and S_{PO_4-P} were determined as above for field measurements. pH measurements were made immediately before a filtered sample was taken, by the use of a constant time (2 minutes), no stirring technique. Concentrations of magnesium, ammonium, and phosphate used in this experiment are presented in Table 2. These conditions were chosen to ensure solution saturation in all flasks and thereby simulate field conditions where precipitation was observed. Samples had ionic strengths of approximately 0.09M.

TABLE 2 - Initial concentrations used in this experiment

Species	Concentration (ppm)	Concentration (mM)	Starting Salt
Magnesium	170	7.0	$MgCl_2 \cdot 6H_2O$
Ammoniacal Nitrogen (N)	1830	131	NH_4Cl
Orthophosphate (P)	65	2.1	KH_2PO_4

Sampling was undertaken between 50 and approximately 200 hours after pH adjustment to between 6.8 and 8.5.

Solids for analysis were recrystallized to remove glass by dissolution in H_2SO_4, filtration and recrystallization with NaOH. Characterization of the dried, recrystallized solid precipitate was by Fourier Transform Infra-Red spectrophotometry, X-Ray Diffractometry and Electron Microscopy (EM). Samples were analysed for water content by Karl Fischer titration and the solid was found to have a water content of 12.2±0.9%.

RESULTS and DISCUSSION

Field measurements

Table 3 summarizes the extremes of concentration, pH, $-\log_{10}(Q_s)$ and temperature determined in the field.

Measurements were made in mid-Autumn climatic conditions, and it would be expected that these parameters would vary through the other seasons, due to changes in lagoon performance. It should be pointed out that this Q_s is not necessarily an equilibrium situation, as in the case of P$_s$ (see Nomenclature). It has been derived and included here, to be used for comparison with the experimental P$_s$ results to fulfill the aims of this paper.

Laboratory determinations of P$_s$

Solid analysis using the methods indicated above verified the presence of struvite as the solid constituent of reaction flasks. The loss of ammonia from solution may affect the determination of P$_s$, particularly in solutions of higher pH (Taylor et al. (1963)). This effect is somewhat buffered in the system studied by (i) high ammoniacal nitrogen concentrations in all samples, thereby damping the effect of any loss, and (ii) relatively low pH values and therefore less volatilization of NH_3 from solution.

TABLE 3 - Summary of field data measurements

Measurement	Field Site			
	1	2	3	4
Magnesium (ppm)				
$\overline{S_{Mg}}$	67	63	60	49
$\sigma_{S_{Mg}}$	14	18	11	4
Ammonia-Nitrogen (ppm)				
$\overline{S_{NH_3-N}}$	970	910	980	800
$\sigma_{S_{NH_3-N}}$	445	310	325	225
Orthophosphate (ppm)				
$\overline{S_{PO_4-P}}$	43	37	31	16
$\sigma_{S_{PO_4-P}}$	4.2	7.8	5.9	1.3
pH				
$\overline{pH}$	7.1	7.2	7.6	7.8
σ_{pH}	0.1	0.1	0.1	0.1
Temperature (°C)				
$\overline{T}$	21.9	21.6	20.5	19.6
σ_T	0.7	1.1	2.4	1.7
pQ_s				
$\overline{pQ_s}$	6.6	6.8	6.8	7.2
σ_{pQ_s}	0.3	0.4	0.2	0.1

[1] Inflow to first lagoon

[2] Outflow from first lagoon

[3] Outflow from second lagoon

[4] Outflow from final lagoon

The experiment was conducted at $30°C$ for a number of reasons. Firstly, time constraints caused modification of an original research plan by which experiments at 10 and $20°C$ would also have been conducted (as indicated by Table 3, this would cover the range of temperatures encountered in the field). Another reason was that $30°C$ indicates the most soluble situation for the reacting nutrients, hence the data obtained would show the very least precipitation expected in the lagoon network. Thirdly, the effect of temperature on P_s is small in comparison to factors such as pH and soluble nutrient concentrations.

Soluble phosphate and conditional solubility constant against pH data and least squares equation fits are shown in figures 1 and 2.

The data obtained in this experiment are not in a form that can be immediately compared with the bulk of previous literature on the subject, where results are expressed as pK_{sp} values (Table 1). It agrees with the calculated behaviour of struvite in solution estimated by Verplaetse et al. (1985,1986), Snoeyink and Jenkins (1980) and Stumm and Morgan (1981). Further calculations involving data from this experiment yield an apparent $pK_{sp} = 12.76 \pm 0.56$. This value was obtained using a Fortran-77 computer program which used a simple list of equilibria and constants relevant to struvite formation (Table 4).

Both P_s and S_{PO_4-P} decrease rapidly with an increase in pH from 6.5 to 8.2.
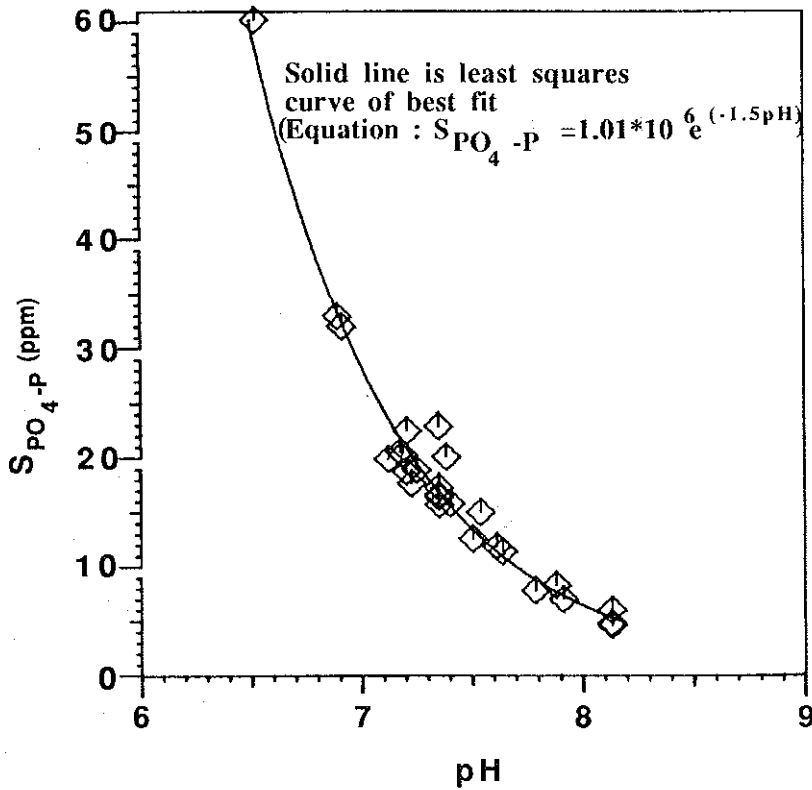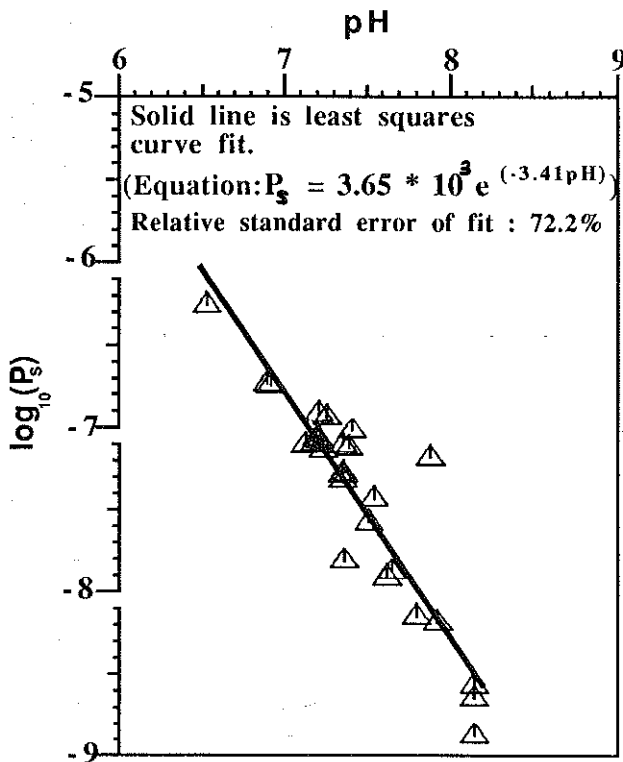
Fig. 1 - Soluble PO_4-P plotted against pH, as determined in laboratory experiments

Solid line is least squares curve of best fit (Equation : $S_{PO_4-P} = 1.01 * 10^6 e^{(-1.5pH)}$)

Fig. 2 - Log of conditional solubility constant (P_s) at different solution pH

Solid line is least squares curve fit.
(Equation: $P_s = 3.65 * 10^3 e^{(-3.41pH)}$)
Relative standard error of fit : 72.2%

TABLE 4 - Equilibrium constants (as pK) used to obtain pK_{sp} from P_s data[1]

| Equilibrium	pK value
$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightleftharpoons MgNH_4PO_4 \cdot 6H_2O$	-12.6
$Mg^{2+} + OH^- \rightleftharpoons Mg(OH)^+$	-11.4
$NH_4^+ \rightleftharpoons NH_3 + H^+$	-9.24
$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	-2.1
$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	-7.2
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	-12.3

[1] source of K values - Sillen 1964

Activity coefficients were assumed to be unity, and a small temperature correction (303/298) was employed to obtain a value at $25°C$. This value is consistent with the previously published values of K_{sp} for struvite at $25°C$ (Table 1). It is lower than the 2 most recent determinations of 13.12 and 13.15 by Burns and Finlayson (1982) and Taylor et al. (1963) respectively. If activity coefficients of 0.9 (the extreme for this data) are used for all ions, the mean value of K_{sp} at $25°$ becomes 12.82 ± 0.56.

Combining the earlier results it is possible to compare the Q_s values obtained in the field and the experimental P_s values. Log values of these quantities are shown in figure 3 for different pH values between 6 and 9.

In considering figure 3, it should be remembered that temperature differentials exist both within the field Q_s data, and between the Q_s and laboratory P_s results (Table 3). From the figure, it is possible to infer at what points the lagoons are likely (through thermodynamic considerations) to form struvite in the present situation. Data from solubility experiments indicate the likelihood of precipitation at sites 2,3 and 4 for some of the time.

Earlier rough calculations of Mg and P balances for the lagoon system at the piggery indicated that there were reductions of these quantities as the wastewater proceeded from lagoon to lagoon. The work reported here has indicated struvite precipitation plays a role in the removal of these from the wastewater, together with the obvious biological processes.

Fig. 3 - Comparison of field $\log_{10}(Q_s)$ (points) and laboratory $\log_{10}(P_s)$ (line) with pH
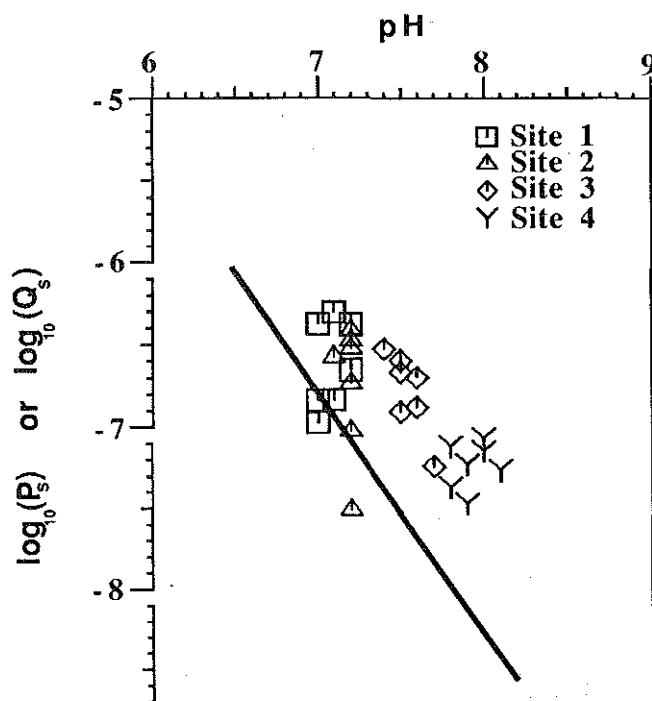
CONCLUSIONS

On the basis of the experimental work reported in this paper, it appears that struvite may form from field site 2 onwards to some extent. Solubility determinations outside of this range of pH require further experimental investigation, as do the effects of high concentrations of non-reacting ions and various other influences on the precipitation from solution of struvite. The correlation between phosphate and pH will be useful as part of a more complete prediction on struvite precipitation that can be expected in the piggery lagoon system. The potential to recover struvite from piggery effluents based on this work looks promising, although further work is required.

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