The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological excess phosphate removal Part 4: Experimental periods using ferric chloride

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Abstract

The effect of simultaneous ferric chloride ($FeCl_3$) dosing on biological phosphorus (P) removal was investigated in an activated sludge system at pilot scale. Additional removal due to chemical precipitation was measured as the difference in system P removal between parallel test and control systems. Both systems strongly exhibited biological excess P removal (BEPR). The extent of P release in the anaerobic reactors of the two systems was compared by mass balance, as one indicator of the "magnitude" of BEPR. Phosphorus fractionation of the mixed liquor also served as an indicator of the biological and chemical mechanisms. Evidence was found that the BEPR mechanism is partially inhibited by simultaneous $FeCl_3$ addition, even in the absence of effluent phosphate limitation. However, the degree of inhibition was relatively low, ranging from 3 to 20% (approximately) for $FeCl_3$ doses in the range ca. 10 to 20 mg/ℓ as Fe, with a system P removal of 20 to 30 mgP/ℓ in the control. $FeCl_3$ dosing in this range was sufficient to produce additional P removal of the order of 2 to 12 mgP/ℓ over periods of one to three sludge ages per experimental period, depending on the point of chemical addition and sludge age of the system. Sustained operation of the BEPR mechanism in the presence of $FeCl_3$ was possible over a continuous period of 7 to 12 sludge ages, under conditions in which effluent phosphate was both non-limiting or limiting. Under effluent P limiting conditions, the chemical and biological mechanisms appear to be "disadvantaged" to approximately the same extent, as evidenced by the apparent stoichiometry of Fe:P for the chemical precipitation and magnitude of the polyP containing fractions measured for the biological mechanism. This suggested that the biological mechanism is able to compete effectively with the chemical mechanism under conditions of low reactor phosphate concentrations (<0.5 mgP/ℓ orthoP) for sustained periods. However, the presence of simultaneous chemical precipitant significantly reduces the extent to which the biological P removal potential is utilised under P-limiting conditions. This could explain the difficulty sometimes reported in the control of full-scale activated sludge systems with simultaneous precipitant addition where a very low effluent P concentration (<1 mgP/ℓ) has to be achieved.

Nomenclature

%ile	Percentile
Δ	Delta, meaning "difference in" or "change in" (e.g. $\Delta M,P_{rem}$)
AE1 or 2	Aerobic zone or reactor
Fe~P~O	Ferric phosphate/ oxide precipitate (theoretical) after ashing of ferric hydroxy-phosphate
Fe~P~OH	Ferric hydroxy-phosphate
Alk.	Alkalinity (unless otherwise stated: bicarbonate alkalinity)
AN	Anaerobic zone or reactor
AX	Anoxic zone or reactor
COD	Chemical oxygen demand
DSVI	Dilute sludge volume index
f	Filtered *(in italics)*
fP_t	Filtered total phosphate
$fP_{t,a}$	Filtered total phosphate, anaerobic zone or reactor
$fP_{t,b1 \text{ or } b2}$	Filtered total phosphate, first or second aerobic zone or reactor, respectively
$fP_{t,d}$	Filtered total phosphate, second anoxic zone or reactor
ISS	Inorganic suspended solids
M,P_{rem}	Mass of phosphate removed (mgP/d)
M,P_{rel}	Mass of phosphate released (mgP/d)
N_{ae}	Concentration of ammonia in the effluent
N_{ai}	Concentration of ammonia in the influent
No_3 or No3	Concentration of nitrate
$No_{3,a}$	Concentration of nitrate in the anaerobic zone/ reactor
$No_{3,b1 \text{ or } b2}$	Concentration of nitrate in the first and second zone/ reactor, respectively
$No_{3,d}$	Concentration of nitrate in the anoxic zone/ reactor
$No_{3,e}$	Concentration of nitrate in the effluent
N_{te}	Effluent TKN concentration
N_{ti}	Influent TKN concentration
orthoP	Orthophosphate
O_t	Oxygen uptake rate (in mg/[ℓ·h])
PCA	Perchloric acid (fractionation studies)
polyP	Polyphosphate
$PO_{4,a}$	OrthoP concentration in the anaerobic zone
$PO_{4,b1}$ or $_{b2}$	OrthoP concentration in the first aerobic (b1) or second aerobic (b2) zone
$PO_{4,d}$	OrthoP concentration in the first anoxic zone
$PO_{4,e}$	OrthoP concentration in the effluent
$PO_{4,i}$	OrthoP concentration in the influent
PSTs	Primary settling tanks (or primary sedimentation tanks)
P_{ti}	Influent total P concentration
P_{te}	Effluent total P concentration
P_{trem}	Total P concentration removed
P_{rel}	Total P concentration released (measured on filtered mixed liquor sample)
Q_i	Influent flow rate
Q_s	RAS (or s) recycle flow rate
rem	Removal/removed
RES	Residue (in fractionation studies)
S_{bsi}	Readily biodegradable soluble COD in the influent

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TABLE 1
Sewage supplement composition by experimental period
(Refer to Table 2 for relevant $FeCl_3$ dose, acid dose and sludge age)

Period Date range	No. of days	Na-acetate mg/ℓ as COD	K_2HPO_4 mgP/ℓ	$MgCl_2$ mg Mg/ℓ	K_2HPO_4 mg K/ℓ	$NaHCO_3$ mg/ℓ as $CaCO_3$
3.3.1 (Ferric) 16/5/95 to 16/7/95 **3.3.1 (b) Sub-period of Period 3.3.1** 16/6/97 to 16/7/95	62 31	150	40	12.6	100	100
3.3.2 (Ferric) 17/7/95 to 19/8/95	34	150	40	12.6	100	100
3.3.3 (Ferric) 8/9/95 to 5/10/95	27	150	40	12.6	100	100
3.3.4 (Ferric) 6/10/95 to 23/10/95	18	150	40	12.6	100	100
3.3.5 (Ferric) 24/10/95 to 3/11/95	21	150	40	12.6	100	100
3.3.6 (Ferric) 14/11/95 to 3/12/95	20	150	40	12.6	100	100
New semi-enhanced culture developed (Ferric dosed) 29/7/97 to 4/8/97 5/8/97 to 8/8/97 9/8/97 to 20/8/97	 7 4 12	 50 75 100	 0 0 0	 12.6 12.6 12.6	 0 0 0	 100 100 100
3.6.1 (Ferric) 21/8/97 to 4/10/97	45	100	0	12.6	0	100
3.6.2a (Ferric) 5/10/97 to 7/12/97	64	100	0	12.6	0	0
3.6.2b (Ferric) 8/12/97 to 20/12/97	13	100	20	12.6	50	0

SD Sample standard deviation
S.G. Specific gravity
S_{te} Effluent (total) COD concentration
S_{ti} Influent (total) COD concentration
S_{usi} Unbiodegradable soluble COD in the influent
SUP Supernatant (in fractionation studies)
TKN Total Kjeldahl nitrogen
TSS Total suspended solids
VSS Volatile suspended solids

Introduction

A literature review in **Part 1** of this series of papers (De Haas et al., 2000a) indicated that $FeCl_3$ is commonly used as simultaneous precipitant in activated sludge systems, including several major wastewater works (WWW) in the Johannesburg area which need to comply with the Special Phosphate Standard (<1 mgP/ℓ as orthoP). In the case of Darvill WWW in KwaZulu-Natal, the same standard applies and simultaneous alum dosing is in use (De Haas et al., 2000c). In 1995, indicative prices from chemical suppliers suggested that a cost benefit could be gained by switching from alum to $FeCl_3$ dosing at Darvill WWW, due to the relatively low cost of $FeCl_3$ generated as a by-product of NaOH and chlorine manufacture in the Johannesburg (Gauteng) area. Excepting transport costs, which differ from area to area, the principal cost saving can be attributed to the relatively large percentage of metal in the iron chloride salts (typically 12 to 15% m/m as Fe in the delivered product, or 2.2 to 2.7 mol Fe/ kg product) compared to aluminium sulphate (typically 4.2 to 4.4% m/m as Al in the delivered product, or approx. 1.6 mol Al/kg product). However, a report in the literature (Lötter, 1991) of ferric salts proving to be inhibitory to the biological P removal process, prompted a cautious approach to changing the chemical dosed at Darvill WWW for augmentation of P removal.

In view of the experience gained from the pilot-plant studies conducted at Darvill WWW to investigate the effect of alum dosing on a biological P removal system (De Haas et al., 2000c), it was logical to extend the study to include the effect of $FeCl_3$. This paper describes the outcome of these studies with $FeCl_3$ as simultaneous precipitant at pilot scale.

Materials and methods

Pilot plant set-up

Two identical pilot-plant units (R1 as test and R2 as control) were set up and operated in the same manner as described in **Part 3** (De Haas et al., 2000c).

Pilot-plant feed supplementation for enhanced cultures

The first period of $FeCl_3$ dosing followed on directly from the last alum dosing period (**Part 3**) although an intervening period of 10 d (half of one sludge age) was allowed during which no chemical dosing occurred. A further equilibration period of 10 d (half of one sludge age) was allowed from the time of commencement of $FeCl_3$ dosing until the experimental results for the first period were reported (Period 3.3.1).

For the $FeCl_3$ dosing periods, the influent supplements were not changed significantly from those used in the alum dosing periods (Part 3). The acetate feed supplement was kept constant throughout at 150 mg/ℓ as COD except for periods with P limitation in which it was reduced to 100 mg/ℓ as COD (Table 1). Similarly, magnesium, potassium, and phosphate concentrations were held constant, except

TABLE 2
Experimental periods of $FeCl_3$ and acid dosing to pilot plants.
Target influent flow rate = 36 ℓ/d throughout.

Period name Date range Comments	No. of days	Zoned dosed with $FeCl_3$/ acid	$FeCl_3$ dose to R1 (test) unit (mmol/d as Fe)	Acid (HCl) dose (mmol/d)	Sludge age Rs (d)
3.3.1: Low $FeCl_3$ 16/5/95 to 16/7/95	62	AE1	6.65	10	20
3.3.1 (b) Subperiod of 3.3.1 16/6/95 to 16/7/95	31				
3.3.2: High $FeCl_3$ 17/7/95 to 19/8/95 Settling problems develop in R1	34	AE1	13.3	10	20
20/8/95 to 29/8/95 Settling problems in R1 worsen	9	AN	13.3	10	20
29/8/95: **R1 mixed liquor discarded due to settling problems. Re-seeded R1 with half of mixed liquor from R2.** Recommenced ferric dosing 3/9/95.	5	AN	6.65	10	20
3.3.3: Low $FeCl_3$ 8/9/95 to 5/10/95 Settling problems re-emerge in R1	27	AN	6.65	10	20
3.3.4: Low $FeCl_3$ 6/10/95 to 23/10/95	18	AN	6.65	10	10
3.3.5: High $FeCl_3$ 24/10/95 to 13/11/95	21	AN	13.3	10	10
3.3.6: High $FeCl_3$ 14/11/95 to 3/12/95	20	AE1	13.3	10	10
New semi-enhanced culture developed, with low ferric dose 29/7/97 to 20/8/97	23	AE1	6.65	0.5	10
3.6.1 Low $FeCl_3$ 21/8/97 to 4/10/97	45	AE1	6.65	0.5	10
3.6.2a Low $FeCl_3$ 5/10/97 to 7/12/97	64	AE1	6.65	0.5	10
3.6.2b Low $FeCl_3$ 8/12/97 to 19/12/97	12	AE1	6.65	0.5	10

where P (and hence K) supplementation was withheld to create P limiting conditions (Table 1). Alkalinity was supplemented in all periods (at 100 mg/ℓ $CaCO_3$) except for two periods when it was deliberately omitted. Hence the main variations in influent composition were those due to the settled sewage sampled from the full-scale works.

$FeCl_3$ and acid dosing

As a point of departure, it was assumed that a molar ratio of 0.5 mol P_{trem}/ mol Fe_{dosed} should be achievable (Wiechers, 1987; Aspegren, 1995). Initial calculations were based on the supplier's minimum specification of 14% (m/m) Fe in the $FeCl_3$ sample received. Dilutions were calculated to give a daily dose to the test reactor of 6.2 mmol Fe/d per 25 mℓ diluted stock solution. Once the $FeCl_3$ sample had been checked for true iron content by atomic absorption spectrometry, it was found to contain 14.97% (m/m) total Fe with an S.G. of 1.46 kg/ℓ. In order to maintain consistency relative to the experimental periods already covered, it was decided to leave the dosage to the reactor unchanged, and to accept the slightly higher actual molar amounts dosed (6.65 mmol Fe/d per 25 mℓ diluted stock solution).

A dilute solution of chemical precipitant in tap water was prepared from the diluted stock solution and dosed into the anaerobic (AN) or first aerobic (AE1) zone of the test reactor (R1) at the rate of 500 mℓ/d. It was found that a small amount of acid was required to prevent coagulation (hydroxide formation) in the diluted solutions of $FeCl_3$ dosed. For this reason, 10 mmol/d of HCl was added to the diluted solution of $FeCl_3$ dosed to R1, and the same amount of acid was fed in tap water only to the control reactor (R2), also at a rate of 500 mℓ/d. The acid dose was equivalent to 14 mg/ℓ as $CaCO_3$ (based on an influent flow rate of 36 ℓ/d), which was considered small in relation to the alkalinity supplement of 100 mg/ℓ as $CaCO_3$ for most periods. *[In later experimental periods, it was found that the amount of acid required to prevent coagulation of the diluted $FeCl_3$ could be further reduced. For Periods 3.6.1 and 3.6.2 in which the sewage alkalinity was not supplemented, the only acid dosed was 0.5 to 1.0 mmol/d in the form of HCl (2 mℓ/ℓ) added to the $FeCl_3$ working stock solution (see Table 2)]*. Table 2 gives the actual dosage rate applied for the respective experimental periods. An iron dose of 6.65 and 13.3 mmol Fe/d into a target influent flow of 36 ℓ/d in the pilot plants corresponds to 30 and 60 mg/ℓ influent as $FeCl_3$ respectively. At a molar ratio of 0.5 mol P_{trem}/ mol Fe_{dosed}, additional P removal of 2.86 and 5.72 mgP/ℓ influent respectively may be expected at these dose rates. This appeared to be a reasonable target for "low" and "high" ferric dosage rates on the basis of full-scale operating experience at Darvill WWW.

TABLE 3
Summary of P removal due to $FeCl_3$ measured in pilot plants.
P_{trem} implies TP removal (Influent - Effluent). R1 : $FeCl_3$ dosed; R2: control.

Period	Data	Fe dose mmol/d	Zone	$P_{trem,R1}$ mgP/ℓ	$P_{trem,R2}$ mgP/ℓ	$\Delta P_{trem,R1} - P_{trem,R2}$ mgP/ℓ	$\Delta M(P_{trem,R1} - P_{trem,R2})$ mgP/d	Observed Stoichiometry mol P_{trem}/ mol Fe_{dosed}
3.3.1	Average	6.65	AE1	27.1	22.9	4.2	144	0.70
	n			43	43	43	43	43
	SD			6.6	6.0	3.2	119	0.58
	95% CL, upper			-	-	-	181	0.88
	95% CL, lower			-	-	-	107	0.52
3.3.1b	Average	6.65	AE1	27.2	21.2	6.0	201	0.98
	n			21	21	21	21	21
	SD			7.8	6.3	3.1	121	0.59
	95% CL, upper			-	-	-	256	1.24
	95% CL, lower			-	-	-	146	0.71
3.3.2	Average	13.3	AE1	33.8	21.8	11.9	417	1.01
	n			23	23	23	23	23
	SD			5.5	5.7	2.2	74	0.18
	95% CL, upper			-	-	-	449	1.09
	95% CL, lower			-	-	-	385	0.93
3.3.3	Average	6.65	AN	28.8	24.3	4.5	170	0.83
	n			19	19	19	19	19
	SD			6.1	6.9	2.5	100	0.49
	95% CL, upper			-	-	-	219	1.06
	95% CL, lower			-	-	-	122	0.59
3.3.4	Average	6.65	AN	31.7	29.4	2.3	75	0.36
	n			12	12	12	12	12
	SD			2.2	4.4	2.7	111	0.54
	95% CL, upper			-	-	-	145	0.71
	95% CL, lower			-	-	-	5	0.02
3.3.5	Average	13.3	AN	34.3	25.0	9.3	346	0.84
	n			15	15	15	15	15
	SD			5.4	5.3	1.7	55	0.13
	95% CL, upper			-	-	-	377	0.91
	95% CL, lower			-	-	-	316	0.77
3.3.6	Average	13.3	AE1	31.1	25.0	6.0	211	0.51
	n			12	12	12	12	12
	SD			5.6	6.9	1.8	73	0.18
	95% CL, upper			-	-	-	257	0.62
	95% CL, lower			-	-	-	164	0.40
3.6.1 P limited	Average	6.65	AE1	9.9	10.0	-0.1	-1	0.00
	n			27	32	27	27	27
	SD			2.1	2.0	0.2	11	0.05
	95% CL, upper			-	-	-	4	0.02
	95% CL, lower			-	-	-	-5	-0.02
3.6.2a P limited	Average	6.65	AE1	9.9	9.8	0.1	7	0.03
	n			43	43	43	43	43
	SD			3.0	3.3	0.9	41	0.20
	95% CL, upper			-	-	-	19	0.09
	95% CL, lower			-	-	-	-6	-0.03
3.6.2b P limit lifted	Average	6.65	AE1	15.4	14.7	0.7	32	0.16
	n			10	10	10	10	10
	SD			6.3	7.5	1.8	59	0.29
	95% CL, upper			-	-	-	74	0.34
	95% CL, lower			-	-	-	-10	-0.03

n: no. of observations; SD: Standard deviation; CL: Confidence limit

Parameters measured

All parameters were measured in the same manner as described in **Part 3** of this series of papers (De Haas et al., 2000c).

Chemical fractionation of sludge samples

Fractionation and P release batch tests was carried out according to the procedure described in Table 9 of **Part 2** of this series of papers (De Haas et al., 2000b).

Results and discussion

Results for $FeCl_3$ dosing with influent phosphate and alkalinity supplements

A summary of the results for the $FeCl_3$ dosing periods is given in Table 3.

With few exceptions, total P removal was greater in R1 (ferric dosed) than R2 (control), at both low and high $FeCl_3$ doses. Where phosphate was not limiting (i.e. effluent contained well in excess of 1 mgP/ℓ soluble P), $FeCl_3$ did produce a net improvement in P removal. However, some difficulties were experienced with maintaining "steady state" in the experimental units due to variations in the influent COD from different batches of sewage obtained from Darvill WWW. This, coupled with the comparatively small $FeCl_3$ dose in relation to biological P removal by the "semi-enhanced" cultures, led to a large variance (or standard deviation) in apparent molar ratio of P_{trem}: Fe_{dosed} (Table 3). The variance in the ratio was smaller for Periods 3.3.5 and 3.3.6 when the $FeCl_3$ dose was higher. Interestingly, periods with effluent P limitation showed almost no net additional P removal; these results are discussed separately below.

Mass balances

Overall mass balances for COD, N and P

The overall mass balances (**Appendix A**, Table A3) were satisfactory (100% ± 15) for most periods, but showed inconsistencies in some cases which appeared to be the result of a combination of sampling and measurement errors. Specifically in the case of nitrogen, the mass balances for Periods 3.3.4 through 3.3.6 appeared to be consistently greater than 100%, ranging from 118 to 153%. This problem may have stemmed from under-recovery of influent TKN (possibly due to incomplete digestion). By adjusting all the influent TKN data upwards by 25% (underlined figures in Table A3), recoveries improved (range 94 to 122%). An alternative explanation for the nitrogen mass balance problems may be the sensitivity of the balance to the nitrate results obtained, particularly for the anoxic reactor. *[For example, one set of results (Period 3.3.6, R2, anoxic zone nitrate) was 4.7 mgN/ℓ. This was not consistent with an average of 2.2 mgN/ℓ for the preceding two periods; when this result was assumed to be 2.2 mgN/ℓ the mass balance improved from 61% to 99%. Investigation of the extent of denitrification in relation to P uptake in the anoxic zone fell beyond the scope of the present study].*

P mass balance around the anaerobic reactor

From mass balance considerations around the anaerobic reactor it can be shown that:

$$M,P_{rel} = [(Q_i + Q_s).\, fP_{t,a}] - [Q_i.P_{ti} + Q_s.P_{te}] \qquad (4.1)$$

TABLE 4
Comparison of P release in anaerobic reactors (on mass basis) between R1 and R2, expressed as a percentage (R1/R2)

Period	$M(P_{rel,R1})/M(P_{rel,R2})$, %				
	Mean	SD	n	95% upper confidence limit	95% lower confidence limit
3.3.1	88	3.4	18	89	86
3.3.2	97	14.4	9	103	86
3.3.3	93	6.0	4	103	84
3.3.4	89	6.6	5	97	81
3.3.5	87	16.0	5	107	67
3.3.6	81	8.4	4	94	68
3.6.1	51	9.6	14	60	41
3.6.2a	50	5.5	22	69	30
3.6.2b	45	9.9	5	50	41

SD: Standard deviation; n: no. of observations

where:

M,P_{rel} is the mass of P released to the (filtered) supernatant in the anaerobic zone.

Using the measured data given in Tables A2 and A3 (Appendix A) and Eq. (4.1) with $Q_i = Q_s$ (1:1 s-recycle ratio), P release in the anaerobic zone of the test unit (R1) could be calculated and expressed as a percentage of that in the control unit. The results are given in Table 4.

The data in Table 4 suggest that P release in the anaerobic zone of the test unit was inhibited to some degree by the dosing of $FeCl_3$. Again, variance in the data was relatively large, as indicated by the 95% confidence limits (Table 4). Nevertheless there appeared to be a trend in that either prolonged dosing (Periods 3.3.2 to 3.3.4 covered more than four sludge ages) or higher $FeCl_3$ doses (Periods 3.3.5 and 3.3.6) produced more inhibition of P release in the anaerobic reactor. Also, when P was limiting and effluent P concentrations low (Periods 3.6.1 and 3.6.2a), the biological mechanism was clearly inhibited (or "depressed") in the presence of $FeCl_3$ (Fig. 2). In Period 3.6.2b, influent P was increased but the recovery of the biological mechanism was not seen in the P release results, probably because this experimental period was short (12 d). This period is discussed further below.

Molar ratios of P removed/ Fe dosed and point of dosing

Calculation of the average molar ratio of P removal/ Fe dosed in Table 3 is based on the assumption that the difference in system P removal between R1 (test) and R2 (control) is only ascribable to chemical addition. A problem with this assumption is that effects of both chemical and biological origin are lumped: if the biological mechanism is weaker in R1 than R2, it will reflect as a lower P (removal)/ Fe molar ratio and could be confused with a weaker chemical precipitation mechanism. Nevertheless, it is interesting to compare the net additional P removal ($\Delta P_{trem} = P_{trem,R1} - P_{trem,R2}$) in Table 3 for respective periods at the same $FeCl_3$ dose but different sludge ages (20 d vs. 10 d), Table 5. For Periods 3.6.1 and 3.6.2a,

Table 5
Comparison of estimated P:Fe stoichiometry at different sludge ages

$FeCl_3$ dose Zone dosed	Periods	Sludge age R_s, d	Data source	mol P/ mol Fe	Ratio R_s 20d/ R_s 10d
Low, 30 mg/ℓ, AE1	3.3.1 3.6.1 & 3.6.2a	20 10	Table 3 Fractionation *	0.72 0.40	**1.8**
Low, 30 mg/ℓ, AE1	3.3.1(b) 3.6.1 & 3.6.2a	20 10	Table 3 Fractionation *	0.98 0.40	**2.5**
Low, 30 mg/ℓ, AN	3.3.3 3.3.4	20 10	Table 3 Table 3	0.83 0.36	**2.3**
High, 60 mg/ℓ, AE1	3.3.2 3.3.6	20 20	Table 3 Table 3	1.01 0.51	**2.0**

* Fractionation data from Table 7.

during which P-limitation occurred in both units, the P:Fe stoichiometry in Table 3 does not apply since virtually complete P removal occurred in both units. For these periods, the stoichiometry was estimated from fractionation results (Table 7).

Rabinowitz and Marais (1980) proposed that the chemical P removal mechanism involves the formation of iron hydroxide for at least a part of the iron dosed, and that ion exchange between phosphate and hydroxyl ions occurs as a slow competing side reaction to the rapid direct precipitation of iron phosphate. Accepting this hypothesis, ferric hydroxide may be expected to accumulate in the mixed liquor, thereby producing a so-called "persistence effect". Arising from this effect, the mixed liquor has a residual chemical P removal potential after metal dosing is stopped. Similarly, when the influent loads vary, fluctuations in effluent P concentration are attenuated despite a constant metal dose. Hence, for the same metal dose, chemical P removal should be more efficient (i.e. greater ratio of P_{trem}/ Fe_{dosed}) at a longer sludge age where the longer solids retention time would allow the PO_4^{3-}/OH^- ion exchange reaction to proceed closer to completion. The results in Table 5 appear to support this hypothesis, since the additional (i.e. chemical) P removal was greater for the periods at a 20 d sludge age, relative to 10 d. The ratio between the paired results was approximately 2, suggesting that the same iron dose was twice as efficient with double the solids retention time.

It can be concluded that the measured system P removal (Table 3) may not be reliable as an indicator of precipitation stoichiometry. The difference in system P removal between the test (R1) and control (R2) units is a measure of the combined chemical and biological removal. Hence, for example, at low effluent P concentrations (Periods 3.6.1 and 3.6.2a), with mean effluent orthoP concentrations of <0.5 mgP/ℓ, the apparent "precipitation efficiency" is greatly reduced, to the point that the system P removal in the test (R1) system dosed with iron is equivalent to or less than that of the control (R2). This may be partly due to inhibition of the biological mechanism but partly also due to chemical precipitation being less efficient at low P concentrations. For this reason, fractionation of the mixed liquor was applied as an independent method of estimating the sizes of the chemical and biological phosphate "pools".

Alkalinity and pH considerations

The acidity of $FeCl_3$ (0.5 to 1% free acid as HCl) *[as supplied by NCP Ultrafloc (Johannesburg)]* as well as alkalinity consumed in the precipitation process may be significant in applications with low alkalinity influent wastewater. In this study it was found that the effluent bicarbonate alkalinity in R1 (test, $FeCl_3$ dosed) was consistently lower than in R2 (control), and the difference was always in the range 20 to 40 mg/ℓ as $CaCO_3$ (Table A1, **Appendix A**). For Period 3.3.1 through 3.3.6, alkalinity consumption due to $FeCl_3$ dosing was approx. 0.66 mg as $CaCO_3$/mg $FeCl_3$, which is less than the theoretical value of 0.92 on the same basis for the precipitation of ferric hydroxide (Loewenthal et al., 1986). For Periods 3.6.1 and 3.6.2a (low effluent P) the alkalinity consumption was approx. 0.8 to 1.17 mg as $CaCO_3$/mg $FeCl_3$, which is closer to the theoretical value for ferric hydroxide. These data suggest that metal phosphate precipitation always precipitated some alkalinity (probably hydroxide), and that the molar ratio Fe_{dosed}:$Alk_{removed}$ increases as that for Fe_{dosed}: $P_{removed}$ decreases.

Various empirical formulae have been put forward in the literature to describe the overall precipitation stoichiometry observed. For example, Luedecke et al. (1989) suggested a general formula for ferric hydroxy-phosphate, namely:

$$Fe_rPO_4(OH)_{3r-3}$$

Luedecke et al. (1989) reported values for r in the range approximately 1 to 2 mol Fe/mol P for residual phosphate concentrations of approx. 1 to 5 mgP/ℓ. For an Fe:P molar ratio of the order of 0.6 mol P/ mol Fe dosed (for non- P limiting conditions, based on fractionation data from this study), the average formula of the precipitate according to Luedecke et al. (1989) would be:

$$Fe_{1.66}PO_4(OH)_2$$

However, this formula predicts an alkalinity loss of only 1.2 mol/ mol Fe (or ~0.4 mg $CaCO_3$/mg $FeCl_3$), which is less than that observed experimentally here. In order to be consistent with the observed alkalinity losses, the general formula for periods without P limitation could be written as:

$$Fe_{1.66}(X^{2+})PO_4(OH)_4$$

where X^{2+} is some unknown (possibly divalent) cation (e.g. Mg^{2+} or Ca^{2+}) (Arvin, 1985; Henze et al., 1992). Under P limiting conditions, the average P:Fe stoichiometry estimated from fractionation data was in the range 0.32 to 0.46 mol P/mol Fe and bicarbonate alkalinity consumption was approx. 2.6 to 3.6 mol

TABLE 6
Fractionation data for periods of $FeCl_3$ dosing without P limitation. Percentages in parentheses are relative contributions to total P of mixed liquor solids (i.e. sum of extracts, including residue (RES) fraction but excluding supernatant (SUP) fraction)

Date, Unit	Period	Ferric dose, zone dosed Low = 30 mg/ℓ High = 60 mg/ℓ as $FeCl_3$ based on influent see Table 2	PCA Complex P mgP/gVSS "Biological"	NaOH Complex P mgP/gVSS "Biological"	Sum of PCA and RES Complex P fractions mgP/gVSS` Note 1 Total " Biological"	Sum of PCA and NaOH orthoP fractions mgP/gVSS Note 1 "Chemical"	VSS during fractionation g/ℓ	Inhibition (-) or stimulation (+) of biological fractions (PCA + RES) % (R1/R2) Note 2	Inhibition (-) or stimulation (+) of biological PCA fraction only % (R1/R2) Note 2
8/6/95, R1	3.3.1	Low, AE1	74.09	*51.23* *	***125.32 ** (67%)	59.62 * *(32%)*	2.568	*-16%* *	*-39%*
8/6/95, R2		-	121.17	*28.46* *	*149.63** (88%)	19.57* *(12%)*	2.674	-	-
4/7/95, R1	3.3.1b	Low, AE1	99.80	*41.56* *	***141.36 ** (69%)	60.38 * *(30%)*	2.396	*-6%* *	*-20%*
4/7/95, R2		-	125.37	*25.22* *	*150.59* (89%)	17.46 * *(10%)*	2.499	-	-
18/7/95, R1	3.3.1b	Low, AE1	118.19	38.39	**156.58** (69%)	68.16 (30%)	2.184	0%	-18%
18/7/95, R2		-	144.30	12.05	156.35 (89%)	18.70 (11%)	2.675	-	-
15/8/95, R1	3.3.2	High, AE1	35.19	129.22	**164.41** (64%)	88.27 (35%)	2.577	-7%	-77%
15/8/95, R2		-	153.59	22.98	176.57 (89%)	20.98 (11%)	2.453	-	-
5/10/95, R1	3.3.3	Low, AN	95.08	40.08	**135.16** (72%)	50.92 (27%)	2.360	-11%	-26%
5/10/95, R2		-	128.37	23.27	151.74 (87%)	21.17 (12%)	2.429	-	-

* : Estimate (for cases where NaOH extraction had not been introduced) based on projected NaOH orthoP and Residue TP fractions (from cases where NaOH extraction had been used).
Note 1: (%) Percentages in parentheses refer to % sum of "Total Biological" and "Chemical".
Note 2: Percentages, e.g. -5%, refer to percent inhibition of R1 fractions, relative to R2.

Alk./ mol Fe. For these periods, the average formula for ferric hydroxy-phosphate complex formed could lie in the following approximate range:

$$Fe_3 (X^{2+}) PO_4 (OH)_8 \quad \text{to} \quad Fe_{2.33} (X^{2+})_{2.5} PO_4 (OH)_9$$

Fractionation studies

Fractionation studies for Periods 3.3.1 through 3.3.3 (Table 6) showed that $FeCl_3$ increased the orthoP ("chemical precipitate") fraction of the sludge by three- to fourfold such that it came to represent about 26% of the sludge total P at the low ferric dose, and 31% of the total P at the high ferric dose. With ferric dosing, the acid extractable (PCA) complex P fraction decreased in size (by 18 to 39% at low ferric doses) but the residue (or alkaline extractable) complex P fraction increased. Most of this residue (or "non cold PCA-extractable" complex P) was in fact alkaline-extractable complex P. The increased size of this fraction was particularly noticeable at high ferric doses, when it predominated.

In **Part 2** of this series of papers (De Haas et al., 2000b) it was concluded that the distribution of complex P between the PCA and NaOH extracts appears to be an artefact of the fractionation procedure and therefore of little significance in the biological mechanism *per se*. Significance should therefore only be attached to the sum of the complex P fractions (acid + alkaline-extractable) as a measure of the biologically stored phosphate in the system. In order to determine the extent to which the NaOH complex P fraction was "biologically active", the results of the batch P release tests were considered. It was found that a significant part of the biologically active P came from complex P extracted with NaOH and this fraction increased in the presence of $FeCl_3$ dosing. If all the NaOH complex P is taken to be of biological origin, then the data in Table 6 suggest that the biological mechanism was never depressed by more than 17% relative to the control for periods without P limitation. In some cases, the size of the biological fractions of the two units appeared to be the same in the test and control units. However, the sum of the biological and chemical fractions was always greater in the test unit, compared to the

TABLE 7
Estimation of molar ratio of additional P removed as chemical precipitate (PCA and NaOH extract orthoP fractions) versus iron dosed as $FeCl_3$.
**** Italics = estimate of NaOH orthoP fraction where this step was not carried out***

Unit/Ferric	Date	PCA + NaOH orthoP fractions * mgP/gVSS	Ave. VSS for Period g/ℓ	VSS wasted g/d	PCA + NaOH orthoP wasted mgP/d	Difference (R1-R2) PCA +NaOH orthoP wasted mgP/d	Fe dosed mmol/d	mol P /mol Fe (This table)	mol P /mol Fe (Table 3)
Without P limitation									
R1: Low Fe: 3.3.1	8/6/95	*59.26*	2.238	3.5818	*212.19*	*137.12*	6.65	0.67	1.02
R2: 3.3.1	8/6/95	*19.54*	2.401	3.8426	*75.06*				
R1: Low Fe, AE 1: 3.3.1	4/7/95	*60.30*	2.238	3.5818	*215.93*	*148.93*	6.65	0.72	1.02
R2: 3.3.1	4/7/95	*17.44*	2.401	3.842	*67.00*				
R1: High Fe, AE1: 3.3.2	15/8/95	88.27	2.357	3.771	332.88	248.66	13.3	0.60	1.03
R2: 3.3.2	15/8/95	20.98	2.509	4.014	84.22				
R1: Low Fe, AN: 3.3.3	5/10/95	50.92	2.437	3.899	198.55	116.44	6.65	0.57	0.82
R2: 3.3.3	5/10/95	21.17	2.424	3.878	82.11				
With P limitation									
R1: Low Fe, AE 1: 3.6.1	8/9/97	25.79	1.291	4.1312	106.54	66.20	6.65	0.32	-0.03
R2: 3.6.1	8/9/97	10.35	1.218	3.8976	40.34				
R1: Low Fe, AE 1: 3.6.1	29/9/97	31.62	1.291	4.1312	130.63	90.60	6.65	0.44	-0.03
R2: 3.6.1	29/9/97	10.27	1.218	3.8976	40.03				
R1: Low Fe, AE 1: 3.6.2a	31/10/97	30.32	1.223	3.9136	118.66	81.43	6.65	0.40	0.04
R2: 3.6.2a	31/10/97	9.81	1.186	3.7952	37.23				
R1: Low Fe, AE 1: 3.6.2a	4/12/97	33.14	1.223	3.9136	129.70	94.29	6.65	0.46	0.04
R2: 3.6.2a	4/12/97	9.33	1.186	3.7952	35.41				

control, which is in agreement with the observations of greater system total P removal in the test unit.

Batch P release tests (data not shown for brevity) showed that the net P release to the supernatant in the presence of excess acetate from the test unit (R1) was depressed by 7 to 15% relative to the control, for periods without P limitation. Similarly, the net P change (or sum of release and uptake) in the respective fractions implied that P release from R1 (test) was depressed by 11 to 26%, compared with the control (R2). Taking account of the apparent uptake in the PCA orthoP fraction by counting it as part of the total biological P release, the total release of P from the sludge was never depressed by more than 7%, relative to the control. On the same basis, one mixed liquor sample taken at high ferric dose from the test unit (15/8/95) showed significantly more total release of P (~20% more than the control).

In summary, iron dosing in the absence of P limitation, usually resulted in partial "inhibition" of the biological P removal mechanism. However, the degree of inhibition was small (~7 to 26%, depending on dose and the method of calculation). The fractionation results for P-limiting conditions were somewhat different and are discussed separately below.

Table 7 compares the additional P removal as chemical precipitate with the metal dose on a molar basis, as estimated from the sludge orthoP fractionation data. For periods without P limitation, it can be seen that the P removal attributable to chemical precipitate (extracted in the PCA + NaOH orthoP fractions) only accounted for about 60 to 70% of the molar ratio observed from P_{trem}/Fe_{dosed} (Table 3). The fractionation procedure used here lacked the sophistication necessary to distinguish between different forms of chemically bound orthoP. According to the hypothesis of Rabinowitz and Marais (1980), iron dosing gives rise not only to ferric phosphate precipitate directly, but also to ferric hydroxide as an ancillary precipitate. The latter also has chemical P removal potential due to ion exchange reactions. Most likely, this ferric hydroxide exists in colloidal/ amorphous form and may be bound to components ("microfibrils") of the biomass such as extracellular polysaccharide (Brown and Lester, 1979; He et al., 1996). If the resultant ferric hydroxy-phosphate colloid is similarly bound to biomass particles and not fully solubilised in cold PCA or NaOH at room temperature, it could account for the failure of the fractionation method to completely recover the chemical phosphate fraction. It is worth noting that evidence of a "reserve" chemical precipitation potential (the so-called "persistence effect" ascribed to ferric hydroxide by Rabinowitz and Marais, 1980) was found in the batch tests using samples of mixed liquor from the test unit which had either been exposed to a relatively high dose of $FeCl_3$ (e.g. Period 3.3.2), or to $FeCl_3$ dosing for a protracted time (Period 3.3.3). Comparing the fractionation patterns before and after the batch P release test, it was observed that a net increase in the PCA orthoP fraction occurred, particularly for the mixed liquor from the test unit (data not shown for brevity). This suggests that a portion of the colloidal iron (from the ferric hydroxide "reserve" in the mixed liquor) reacted with P released biologically from the cells to form ferric phosphate precipitate.

Sludge production

In terms of VSS production, the test (R1) and control (R2) units were comparable for most experimental periods. Period 3.3.6 (20 mg/ℓ Fe dosed to aerobic zone) showed the biggest difference

TABLE 8
Comparison of observed ISS and that predicted from chemical P removal for $FeCl_3$ dosing periods.
Fe~P~OH : hypothetical metal hydroxy-phosphate, $Fe_r PO_4 OH_{(3r-3)}$
Fe~P~O : hypothetical metal phosphate oxide, $Fe_r PO_4 O_{(1.5r - 1.5)}$

Period (Duration): $FeCl_3$ dose	Stoichiometry Observed Table 3	Estimate from *Stoichiometry Observed*	Estimated ΔISS from *Stoichiometry Observed*	Δ ISS Observed	Error (Estimate-Observed)
	mol P_{rem}: mol Fe_{dosed}	*Fe~P~OH*	*Fe~P~O*	mg/ℓ	*% of MLSS* in R1
Unit:	P:Fe	mg/ℓ	mg/ℓ	R1-R2	%
3.3.1 (62 d): Low Fe dose, AE1	0.72	572	**541**	301	6%
3.3.1(b) (31 d): Low Fe dose, AE1	1.02	632	**634**	376	6%
3.3.2 (34 d): High Fe dose, AE1	1.03	1260	**1266**	771	9%
3.3.3 (27 d): Low Fe dose, AN	0.82	592	**572**	379	4%
3.3.4 (18 d): Low Fe dose, AN	0.37	257	**221**	285	-2%
3.3.5 (21 d): High Fe dose, AN	0.80	617	**594**	396	6%
3.3.6 (20 d): High Fe dose, AE1	0.52	503	**453**	598	-5%
3.6.1 (44 d): Low Fe dose, AE1	0.38*	257	**223**	198	5%
3.6.2a (64 d): Low Fe dose, AE1	0.40*	254	**221**	174	4%

AN = Anaerobic zone; AE1 = First aerobic zone
* Stoichiometry from fractionation data in the case of Periods 3.6.1 and 3.6.2a.

between the two units, with 14% more VSS in R1 than R2 (Table A2, Appendix A). It may be significant that this period had a high iron dose and came after a period of 71 d sustained iron dosing to the same enhanced culture. Under conditions of P-limitation, Periods 3.6.1 and 3.6.2a (low Fe dose to aerobic zone) showed small VSS differences, in the range 3 to 7% more VSS in R1 than R2. It is not possible to say exactly what gave rise to the VSS differences, but an accumulation of chemical precipitate with coagulant properties toward organic material is suggested by the data. One possibility is that the iron (hydroxide) precipitate has properties which adsorb/ enmesh colloidal organic material in a manner that tends to make it unbiodegradable and thus contributing directly to the VSS of the system. The effect would be analogous to an increase in the influent unbiodegradable particulate COD fraction.

In terms of TSS (i.e. MLSS) the test unit showed a significant increase (9 to 33%) in sludge production, particularly at the shorter sludge age of 10 d (Table A2, Appendix A). These results must be viewed in the context of additional P removal as a result of chemical precipitation, with the chemical precipitate contributing to the inorganic suspended solids (ISS).

From the measured mixed liquor VSS and TSS data, the difference in mixed liquor ISS (ΔISS) between the two units was calculated. The observed ΔISS was then compared with estimates of precipitate formation based on the additional P removal in R1 (ΔP_{rem} in Table 3) and the Fe:P stoichiometry of the precipitate, either assumed or estimated. For periods without P limitation, the stoichiometry from Table 3 was accepted (i.e. it was assumed that inhibition of the biological removal mechanism was negligible). *[From fractionation results this was not strictly true. ISS production may be overestimated by this method since an apparently higher Fe:P (lower P:Fe) stoichiometry will result from partial inhibition of bio-P removal]*. In the case of periods with P-limitation, the P:Fe stoichiometry calculated by difference in system P removal was very low (Table 3). Hence, the estimates of Fe:P stoichiometry from fractionation data were accepted for these periods.

In order to relate the predicted precipitate formation with observed differences in ISS, allowance must be made for the conversion of ferric hydroxide (or ferric hydroxy-phosphate, Fe~P~OH) to ferric oxide (or ferric phosphate + ferric oxide, designated Fe~P~O) upon ashing in the VSS test. Table 8 gives a comparison of the observed ΔISS and that estimated from apparent precipitate stoichiometry. It can be seen that the estimates of ΔISS from precipitation stoichiometry show a degree of similarity to the observed ΔISS. The recovery of estimated ISS was in the range 76 to 180% of the observed values. Errors may have arisen from the experimental systems not operating at steady state during all periods. The TSS and VSS concentrations can be expected to take several sludge ages to reach steady state. Over-estimation of ISS in the test unit from apparent Fe:P stoichiometry may also have contributed to the discrepancy relative to observed ΔISS. Despite these discrepancies, the results in Table 8 suggest that the increase in ISS due to chemical dosing may be estimated reasonably accurately (to within ~200 mg/ℓ or a median of ~5% of the mixed liquor TSS) using the hypothetical chemical formulae given in Table 8 and the apparent stoichiometry.

$FeCl_3$ dosing under conditions of P limitation

It was hypothesised that the biological P removal mechanism functions less well in the presence of chemical precipitation under conditions where the effluent P concentration is low and potentially limiting. The two mechanisms may then come into "competition" for available phosphate. Such conditions would be representative of full-scale operating conditions where achieving a low effluent P concentration is the objective. Accordingly, experimental Periods 3.6.1 and 3.6.2a were set up in which a moderate amount of sodium acetate (100 mg/ℓ as COD) was added to the influent along with

magnesium ions, but no phosphate (or potassium). Furthermore, the effect of residual system alkalinity was tested: In Period 3.6.1 (with influent bicarbonate supplement), the median effluent alkalinity was 200 to 225 mg/ℓ as $CaCO_3$, while in Period 3.6.2a (without bicarbonate supplement) it was 90 to 100 mg/ℓ as $CaCO_3$. The latter was representative of that usually observed at full-scale at Darvill WWW.

With influent bicarbonate supplement (Period 3.6.1)

The prevailing reactor pH for Period 3.6.1 was pH 7.4 to 7.5 (median) in the aerobic reactors. At this pH, the solubility limit for ferric (hydroxy) phosphate precipitate is expected to be in the region of 0.2 to 0.4 mgP/ℓ as orthoP, due to the formation of soluble iron-P complexes or "ion-pairs" (data not shown - refer to De Haas, 1998). Hence, even with excess iron, it would be theoretically impossible to achieve an effluent orthoP concentration below approximately 0.2 mgP/ℓ. Background iron (or other cation) concentrations in the influent sewage are likely to have set up similar equilibrium constraints in the control reactor (median aerobic reactor pH 7.5 to 7.7).

The theoretical equilibrium solubility limits for phosphate appear to be borne out by the observed data for the experimental systems. Both units R1 and R2 achieved low average effluent orthoP and total P concentrations (both <0.5 mgP/ℓ, see Tables A4a and b) *[The detection limits of the automated molybdate-ascorbic acid methods used here were 0.1 mgP/ℓ as orthoP and 0.5 mgP/ℓ as total P. Results below detection limit were reported as half the detection limit. This will have produced a low bias in the total P results reported here. Only two of the thirty orthoP results (n=28) for R1 in this period were below detection limit, whereas sixteen of the total P results (n=27) for R1 were below detection limit. For R2, twenty of the total P results (n=32) were below detection limit, while for orthoP, eight of the results (n=32) were below detection limit]*. In previous $FeCl_3$ dosing periods without P limitation, the effluent P concentrations were much higher (>10 mgP/ℓ as total P).

Comparing the P release using mass balance considerations for the anaerobic reactors, it was found that, on average, P release in the anaerobic reactor of the test unit was inhibited by 49% relative to the control. Despite a low Fe dose, this represents about twice the maximum degree of inhibition found for $FeCl_3$ at higher effluent P concentrations (Table 4). However, P release to the supernatant may not fully reflect the magnitude (or "strength") of the biological mechanism because some phosphate may be adsorbed/ complexed by accumulated ferric hydroxide in the mixed liquor.

From fractionation, the size of the polyP "pool" in the test and control units may be compared. Figure 1 shows fractionation results for mixed liquor sampled during Period 3.6.1. Taking the sum of the respective PCA and NaOH fractions, the following observations may be made from Fig. 1:

- The total P content of the mixed liquor (sum of all fractions, based on P/VSS) was almost equal in the two units, or slightly lower in the test unit (dosed with $FeCl_3$). This is in agreement with the results for Period 3.6.1 as a whole in which the test unit had a lower P/VSS ratio and gave a slightly lower system P removal (Table A4a, **Appendix A**).
- The magnitude of the complex P (biological) fractions was depressed by 26 to 37% in R1 (test) relative to R2 (control), which is greater than the degree of depression observed for periods in which P was not limiting (Table 6), but less than that suggested from P release in the anaerobic reactors of the two units (49%, Table 4).
- In relative terms, the magnitude of the orthoP fractions was approximately threefold greater in R1 (test, ferric dosed) compared to the R2 (control), which is similar in relative terms to that for non-P limiting conditions (compare with Table 6).
- In absolute terms, the magnitude of orthoP (chemical) fractions was approx. 25 to 40 mgP/gVSS in the test unit (R1) and 10 mgP/gVSS in the control (R2), which is significantly less for both units than that for periods of comparable flow and iron dose without P limitation (compare with Table 6). This provides evidence that the chemical mechanism is less efficient under P limiting conditions and therefore probably does not have a large "competitive advantage" over the biological mechanism under these conditions.
- The relative percentage contributions of the chemical (orthoP) and biological (complex P) fractions to the total P of the mixed liquor solids were only slightly changed in favour of the chemical fractions under P limiting conditions. *[A degree of uncertainty arose due to the significantly higher residue TP in R1 on 29/9/97 (see Fig. 1)]*. That is, under P-limiting conditions the biological mechanism in the test unit (dosed with $FeCl_3$) was depressed at most by an additional 5 to 14% compared to nonP-limiting conditions, while the chemical mechanism gained by no more than this margin. Again this suggests that the biological mechanism is only at a small competitive disadvantage to the chemical mechanism under P-limiting conditions, when compared with non-P-limiting conditions.
- PCA-extractable complex P fractions became very minor or seemed to disappear in R1 (test), but remained fairly significant in R2 (control). Much of the complex P was NaOH-extractable, and this was particularly noticeable in R1. These observations are linked with those reported in Part 2 (De Haas et al., 2000b) where the fractionation pattern for complex P was found to be partly an artefact of the fractionation procedure itself, apparently depending on the availability of metal (Fe^{3+} ions) during the procedure.

Without influent bicarbonate supplement (Period 3.6.2a)

During Period 3.6.2a, both the test (R1) and control (R2) units again achieved low effluent orthoP concentrations (average <0.5 mgP/ℓ – Table A4b) and total P concentrations (average <0.7 mgP/ℓ – Table A4a). *[The detection limits of the automated molybdate-ascorbic acid methods used here were 0.1 mgP/ℓ as orthoP and 0.5 mgP/ℓ as total P. Results below detection limit were reported as half the detection limit, which will have introduced a low bias in the results. In this period, none of the orthoP results for R1 were below detection limit, while in R2 (n=43), 35% of the orthoP results were below detection limit. Half the total P results were below detection limit]*. The reduction in alkalinity had the effect of lowering the aerobic reactor pH in both units by ~0.4 pH units, with the test unit (R1) showing a median pH = 7.0 at the point of dosing (first aerobic reactor). At pH 7.0, the theoretical equilibrium solubility limit for orthoP is likely to be in the range 0.1 to 0.2 mgP/ℓ (De Haas, 1998). The experimental orthoP data therefore suggest that both systems were close to P-limited for most of Period 3.6.2a.

Figure 2 shows fractionation results for mixed liquor sampled during Period 3.6.2a. Again, ignoring the relative sizes of the PCA and NaOH complex P fractions, the following observations may be made:

- The total P of the mixed liquor was approximately the same (80 to 110 mgP/gVSS) as in Period 3.6.1. The magnitude of the

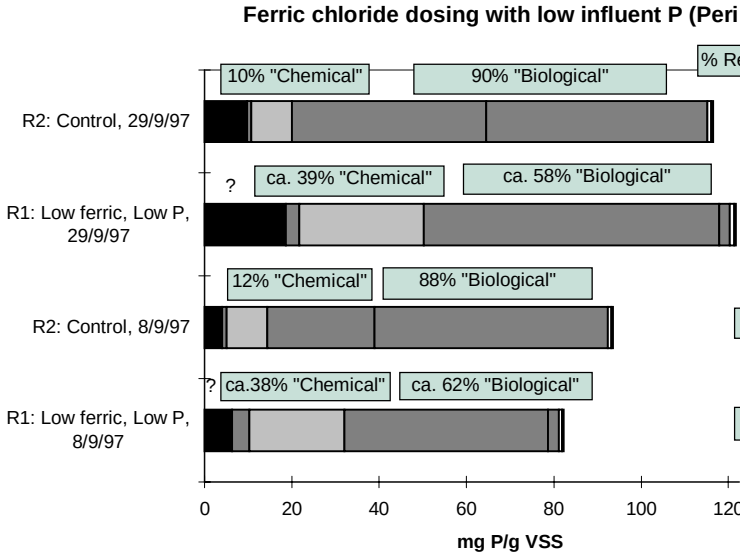

Figure 1
Fractionation data for period of $FeCl_3$ dosing under low influent P conditions with bicarbonate added to influent (Period 3.6.1)

complex P (biological) fractions of the test and control units was also very similar for the two periods:

- The total P content of the mixed liquor was again almost equal in the two units, or slightly lower in the test unit (dosed with $FeCl_3$).
- The magnitude of the complex P (biological) fractions was depressed by 33 to 35% in R1 relative to R2 (control), which is similar to that observed for Period 3.6.1. Again, the degree of depression observed from fractionation data was less than that suggested from mass balance data for P release in the anaerobic reactor (50%).
- Compared with the results for non-P limiting conditions, the relative behaviour of the two units was little changed under P limiting conditions. That is, at most, the biological mechanism may have been further depressed by about 15% in the test unit (dosed with $FeCl_3$), while the chemical mechanism gained by no more than this margin.

Stoichiometry under P-limitation

The stoichiometry of chemical precipitation under P limiting conditions was estimated from fractionation data. By this method, an average stoichiometry of 0.32 to 0.44 mol P/mol Fe (dosed) was found for Period 3.6.1 and 0.40 to 0.46 mol P/mol Fe (dosed) for Period 3.6.2a. These results are somewhat lower than the average result of 0.62 mol P/mol Fe found for non-P-limiting conditions by the same method, reflecting the effect of P-limitation.

Summary for periods with P-limitation

Summarising, Periods 3.6.1 and 3.6.2a represent a fifteen-week experimental period (equivalent to ten sludge ages) during which the pilot plants operated under conditions approximating full-scale conditions with limiting effluent P concentrations. The control unit (R2) achieved virtually complete P removal by biological means alone. The test unit was dosed with $FeCl_3$ at a constant dose of 10 mg/ℓ influent as Fe to the first aerobic reactor. The test unit also achieved virtually complete P removal. Fractionation results indicated that the relative ratio of chemical to biological sludge P fractions in the test unit was similar under P limiting conditions to that when P was not limiting, although a small shift toward the chemical mechanism was noted. It follows that both the biological and chemical P removal mechanisms are "disadvantaged" under P-limiting conditions. However, the chemical precipitation mechanism does limit the extent to which the biological P removal potential can be utilised by removing part of the soluble phosphate in the system. The proportion of P removed by the chemical mechanism is more significant when there is less P in the system (i.e. when P is limiting). This explains why the biological sludge P fractions in the test unit were depressed to a greater degree (relative to the control) under P-limiting conditions, compared to non-P-limiting conditions. The extent of this depression should also be reflected in the extent to which P release in the anaerobic reactor was depressed. The fact that the P release data tended to overestimate the degree of depression of the bio-P mechanism may be a reflection of role played by minor changes in the chemical P fractions in the sludge. It can be speculated that a degree of "exchange" of phosphate occurs between the biological and chemical mechanisms. Particularly under conditions where "surplus" metal hydroxide accumulates in the mixed liquor (e.g. effluent P limiting), P release under anaerobic conditions may give rise to a transient increase in phosphorus complexed in chemical form, followed by a reversal under aerobic (or anoxic) conditions when the equilibrium shifts due to P uptake by the biological mechanism. Some evidence for this was found from fractionation patterns before and after anaerobic batch P release tests (De Haas, 1998).

Finally, both the test and control units operated in a stable manner throughout the fifteen weeks with P limitation. The removal of the alkalinity supplement had no noticeable effect on the systems. It appears that a residual effluent alkalinity of ~100 mg/l $CaCO_3$ is adequate for sustaining stable operation of a BEPR activated sludge system in the presence of simultaneous $FeCl_3$ dosing. There was a tendency for the floc in the test unit to be finer than that in the control, despite a consistently lower DSVI in the test unit. The effluent from the test unit also sometimes showed a tendency to turn slightly turbid. In these respects, the behaviour of the test unit was similar to previous $FeCl_3$ dosing periods, although settleability during Periods 3.6.1 and 3.6.2a never deteriorated to the point that the zone settling velocity was lower in the test unit than the control, as had been the case for earlier experimental periods at a longer sludge age (De Haas, 1998).

Increase in influent P after period of P limitation (Period 3.6.2b)

The effect of an increase in influent phosphate following a prolonged period of P limitation is shown in Figs. 3a and 3b. Initially (during the first week after increased influent P), the test unit (R1, iron

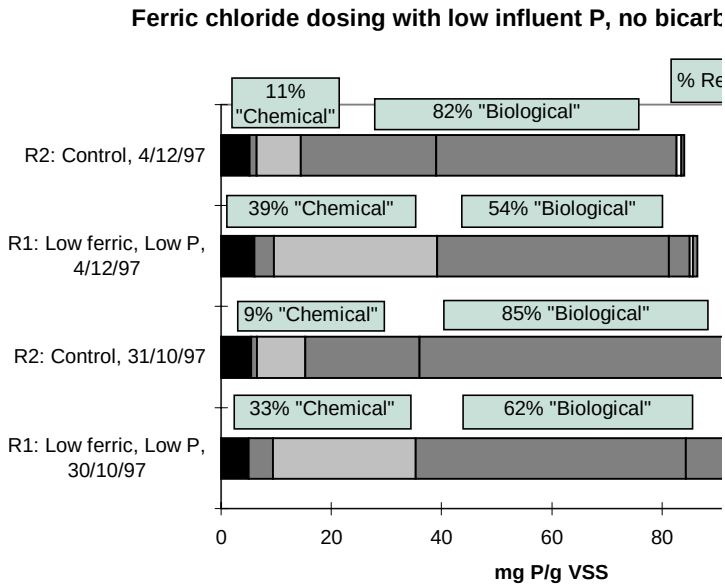

Figure 2

Fractionation data for period of $FeCl_3$ dosing under low influent P conditions without *bicarbonate added to influent (Period 3.6.2a) showed a tendency to turn slightly turbid. In these respects, the behaviour of the test unit was similar to previous $FeCl_3$ dosing periods, although settleability during Periods 3.6.1 and 3.6.2a never deteriorated to the point that the zone settling velocity was lower in the test unit than the control, as had been the case for earlier experimental periods at a longer sludge age (De Haas, 1998).*

dosed), gave a slightly higher effluent P than the control (R2). Therefore iron dosing showed no benefit at this point. This can be ascribed to the fact that the biological P removal mechanism was now less well established in the test unit relative to the control. Hence, "inhibition" (or depression) of bio-P removal as a result of chemical dosing during the preceding period of P limitation became significant when the influent P load was increased. However, the bio-P activity recovered quickly when the influent P load was increased. In the second week after the increase in influent P concentration, the system P removal in the test unit became greater than in the control (Figs. 3a & b). This suggested the onset of a familiar pattern observed under conditions without P limitation, namely, that iron dosing always produced a net greater system P removal in the test unit, relative to the control.

The observations for Periods 3.6.2a and b are similar to those of Aspegren (1995) for a pilot plant (82 m^3/d) operated under real conditions to achieve low effluent P concentrations. A high iron dose in the influent had the effect of increasing the chemical (metal phosphate) fraction of the sludge, but decreasing the bio-P fraction. If it is assumed that precipitation with metal precipitant renders part of the system P unavailable to the BEPR mechanism, simultaneous metal dosing will lead to lower numbers of bio-P bacteria and no net gain in P removal potential in the system. Since the objective of real, full-scale applications is often to achieve effluent orthoP concentrations (e.g. <0.5 mgP/ℓ), these systems must basically be operated under P-limiting conditions (Aspegren, 1995). Under P-limiting conditions, additional metal hydroxide accumulation in the system may be expected. Irrespective of whether direct chemical P precipitation or ion-exchange with metal hydroxide occurs, chemical P removal will most likely be faster than the BEPR mechanism. If precipitation with metal ions has partly replaced BEPR for prolonged periods and low effluent P concentrations (<0.5 mgP/ℓ) are achieved, it may not be possible to increase the BEPR component without experiencing at least a transient increase in effluent P concentrations during the time when the population of bio-P removal organisms increases in number (Aspegren, 1995). The "lost" (or diminished) biological potential therefore cannot be instantaneously re-established when P limitation is lifted. The "spare" chemical removal capacity in the form of metal hydroxide accumulation (the so-called "persistence effect") may not be sufficient to compensate for the diminished biological potential. It follows that the operation of simultaneous precipitation-BEPR processes may be difficult to control under real conditions in order to achieve consistently low effluent P concentrations. This is in agreement with the overall full-scale experience reported by Lötter (1991), and may also partly explain the failure of either alum or iron salts dosing to produce full compliance with the 1 mgP/ℓ orthoP standard at Darvill WWW (De Haas, 1998).

Tertiary chemical precipitation systems following BEPR plants may be advisable where low effluent phosphate concentrations need to be achieved. The advantage is that the BEPR potential of the biological process can be fully realised to justify its capital cost. The disadvantages are: the added capital costs for the tertiary stage; and, without simultaneous metal addition, activated sludge loses the "persistence" effect arising from metal hydroxide accumulation in the mixed liquor (i.e. a buffer against fluctuations in P load is lost). Control of tertiary dosing systems will therefore be more critical to prevent under- or over-dosing.

Conclusions

- In the absence of phosphate limitation, negative interference in the biological P removal mechanism as a result of $FeCl_3$ dosing is detectable but not severe. Using pilot plants in which the effluent phosphate concentrations always exceeded approximately 10 mgP/ℓ, it was found that:
  - A net improvement in P removal was virtually always found in response to $FeCl_3$ addition. At times the additional system P removal approached the 1:1 molar amount expected from the formation of $FePO_4$. On average, the

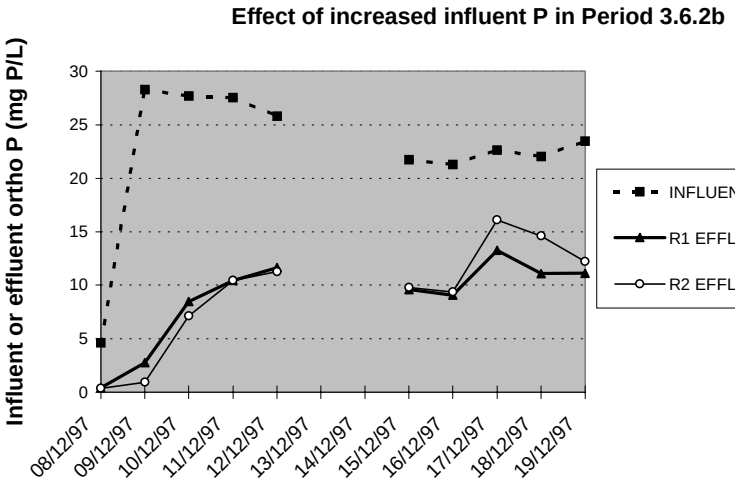

Figure 3a
OrthoP results for Period 3.6.2b (with addition of influent P)

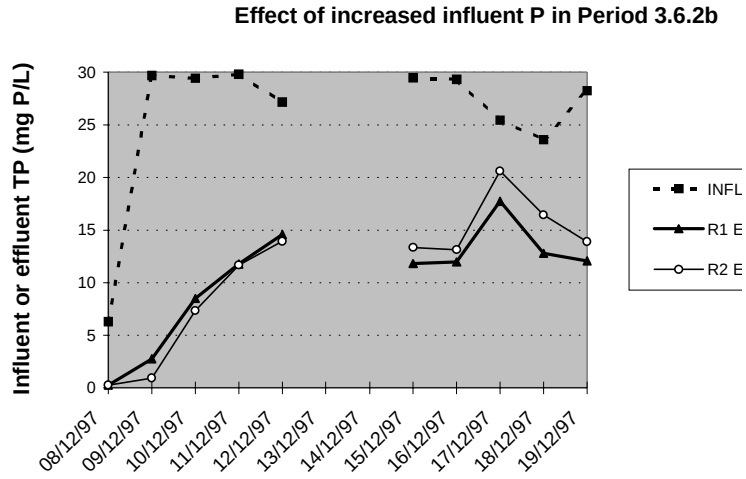

Figure 3b
Total P results for Period 3.6.2b (with addition of influent P)

additional system P removal was approximately 0.75 mol P_{trem} per mol Fe_{dosed}.

- The ratio of additional system P removal to metal dosed is a measure of the overall "precipitation efficiency" since it includes the effect of potential inhibition of the biological P removal mechanism. This may not be a true measure of the stoichiometry, and certainly not where effluent P is limiting. In this study, an estimate of the stoichiometry of precipitation was also obtained from phosphorus fractionation of the mixed liquor. These data suggested that the stoichiometry of the precipitate was closer to 0.62 mol P/ mol Fe. However, by this method, the "chemical" P fraction extracted did not always account fully for the additional system P removal of the test vs. control unit. Part of the chemical P removal may have occurred through PO_4^{3-}/OH^- ion exchange with ferric hydroxide, as proposed by Rabinowitz and Marais (1980). It is likely that this ferric hydroxide/ ferric hydroxy-phosphate precipitate is amorphous or colloidal in nature, and could form a close association with the biomass (e.g. extracellular poly-saccharides or proteins). Such association may have prevented the chemical P component from being fully extracted in the fractionation method applied here.
- Precipitation is more "efficient" at a sludge age of 20 d than at 10 d, giving a higher ratio of P removal to metal dosed. This was in agreement with the ferric hydroxide co-precipitation hypothesis in which the PO_4^{3-}/OH^- ion exchange reaction is considered to be slow compared with the direct precipitation of ferric phosphate. At a longer sludge age, the ion exchange process would be closer to completion.
- Partial inhibition of the biological P removal mechanism as a result of ferric chloride addition was found from fractionation studies and P release in the anaerobic zone of the test unit. However, in the absence of P limitation, the biological mechanism was never depressed by more than about ~20% on average, relative to the control.

- In the presence of phosphate limitation (ie. low effluent P concentrations), inhibition or "depression" of the biological mechanism was greater (about 32% from fractionation data). The P:Fe stoichiometry estimated from fractionation data was also approximately 33% lower under P limiting conditions, compared with non-P-limiting conditions. It was concluded that the biological and chemical P removal mechanisms are "disadvantaged" to approximately the same degree under P-limiting conditions. However, the chemical precipitation mechanism does limit the extent to which the biological excess P removal (BEPR) potential can be utilised by removing part of the soluble phosphate fed to the system.

- The partial loss of BEPR potential in the presence of simultaneous addition chemical phosphate precipitants is expected to be most significant in plants operated at low

(limiting) effluent P concentrations. Tertiary precipitation may be better in such plants. Considering that only minor inhibition of the bio-P removal mechanism was measured under conditions in which effluent P was not limiting (>1 mgP/ℓ), a sustained benefit from simultaneous metal dosing in modified activated sludge systems can nevertheless be achieved where very low effluent soluble P concentrations (say <1 mgP/ℓ) are not required.

- Sludge production was greater in the test unit, with $FeCl_3$ dosing. Minor increases in VSS production (ca. 3 to 14%) were noted, particularly during periods with P-limitation. These changes suggest that iron (or iron hydroxide) affects the coagulation/biodegradation mechanism of activated sludge with organic material. Significant increases in TSS were observed, as expected, due to the additional ISS contributed by chemical precipitate. The observed increase in ISS could be approximately estimated (to within 10% of the TSS in the test unit) on the basis of the stoichiometry observed from differences in system P removal between the test and control unit and a hypothetical general formula for the precipitate.

- Concerning the effect of pH and alkalinity, ferric dosing did not appear to be very sensitive to pH changes in the range of approximately pH 7.0 to 7.7 at the point of dosing, nor to changes in effluent bicarbonate alkalinity in the range approximately 70 to 250 mg/ℓ as $CaCO_3$. Under realistic (i.e. low effluent P) conditions, a drop in aerobic reactor pH at the point of iron dosing from median pH 7.4 to 7.0 did not significantly change the stoichiometry of precipitation estimated from fractionation results. It would appear that a residual effluent alkalinity of approx. (75 to) 100 mg/ℓ $CaCO_3$ is adequate for sustaining stable operation of a BEPR activated sludge system in the presence of simultaneous $FeCl_3$ dosing.

- Using the observed alkalinity changes and fractionation data an estimate of the average formula for precipitation without P limitation was:

  $$Fe_{1.66}\,(X^{2+})\,PO_4\,(OH)_4$$

  where X^{2+} is some unknown (possibly divalent) cation (e.g. Mg^{2+} or Ca^{2+}) (Arvin, 1985). This is the same as the average formula found in **Part 3** for alum (De Haas, 2000c) and corresponds reasonably well with the following general formula used by Luedecke et al. (1989) and Briggs (1996):

  $$Fe_rPO_4\,(OH)_{(3r-3)}$$

  The latter predicts less alkalinity loss per mol Fe. Nevertheless, Luedecke et al. (1989) reported values for r in the range approximately 1 to 2 mol Fe/mol P for residual phosphate concentrations of approx. 1 to 5 mgP/ℓ which are consistent with the stoichiometry observed in this study for non P-limiting conditions.

  The average formula for ferric hydroxy-phosphate formed under P limiting conditions was found to lie in the following approximate range:

  $$Fe_3\,(X^{2+})\,PO4\,(OH)_8 \text{ to } Fe_{2.33}\,(X^{2+})_{2.5}\,PO4\,(OH)_9\,.$$

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TABLE A1
Summary data pH and bicarbonate alkalinity data for periods of $FeCl_3$ dosing

Period	Unit: / Zone:	R1 AN	R2 AN	R1 AE1	R2 AE1	R1 AE2	R2 AE2	R1 H_2CO_3* Alk. mg/ℓ as $CaCO_3$ Effluent	R2 H_2CO_3* Alk. mg/ℓ as $CaCO_3$ Effluent
3.3.1	Min.	6.70	6.59	6.89	6.90	7.15	7.09	185	179
	25%-ile	7.02	6.92	7.29	7.24	7.47	7.46	-	-
	Median	7.09	6.99	7.34	7.29	7.56	7.57	211#	230#
	75%-ile	7.19	7.07	7.42	7.38	7.62	7.64	-	-
	Max.	7.31	7.25	7.55	7.52	7.76	7.88	259	277
3.3.2	Min.	6.85	6.48	7.02	7.03	7.22	7.24	164	202
	25%-ile	6.87	6.80	7.19	7.16	7.43	7.46	-	-
	Median	6.93	6.84	7.23	7.21	7.46	7.50	210#	248#
	75%-ile	6.99	6.88	7.27	7.27	7.53	7.55	-	-
	Max.	7.08	7.00	7.38	7.34	7.62	7.70	260	301
3.3.3	Min.	6.77	6.75	7.19	7.18	7.38	7.37	-	-
	25%-ile	6.91	6.89	7.36	7.33	7.57	7.58	-	-
	Median	7.00	6.99	7.42	7.41	7.66	7.65	241#	256#
	75%-ile	7.06	7.06	7.45	7.46	7.71	7.74	-	-
	Max.	7.30	7.29	7.63	7.88	7.91	8.43	-	-
3.3.4	Min.	6.70	6.48	6.89	6.90	7.15	7.09	-	-
	25%-ile	6.89	6.82	7.21	7.20	7.45	7.46	-	-
	Median	7.00	6.92	7.34	7.29	7.56	7.57	ND	ND
	75%-ile	7.09	7.03	7.42	7.40	7.64	7.68	-	-
	Max.	7.31	7.29	7.63	7.88	7.91	8.43	-	-
3.3.5	Min.	6.77	6.80	7.18	7.22	7.45	7.47	203	243
	25%-ile	6.83	6.85	7.28	7.33	7.48	7.54	-	-
	Median	6.88	6.91	7.34	7.38	7.54	7.61	213#	253#
	75%-ile	7.00	7.09	7.39	7.45	7.61	7.69	-	-
	Max.	7.07	7.21	7.66	7.59	7.97	7.87	219	269
3.3.6	Min.	6.80	6.81	7.20	7.23	7.39	7.44	182	229
	25%-ile	6.96	6.92	7.28	7.37	7.51	7.59	-	-
	Median	7.03	6.96	7.29	7.42	7.54	7.64	212#	250#
	75%-ile	7.05	6.99	7.33	7.46	7.60	7.64	-	-
	Max.	7.30	7.21	7.43	7.63	7.67	7.86	247	273
3.6.1	Min.	7.02	6.98	7.01	7.09	7.13	7.20	159	152
	25%-ile	7.02	7.02	7.12	7.26	7.24	7.45	196	217
	Median	7.27	7.13	7.40	7.50	7.51	7.70	201#	225#
	75%-ile	7.45	7.33	7.54	7.61	7.68	7.79	207	242
	Max.	7.64	7.52	7.67	7.70	7.78	7.87	263	252
3.6.2a	Min.	6.62	6.50	6.59	6.67	6.78	6.86	28	31
	25%-ile	7.02	6.95	7.00	7.05	7.15	7.27	87	126
	Median	7.10	7.00	7.02	7.14	7.20	7.36	97#	132#
	75%-ile	7.14	7.02	7.13	7.22	7.31	7.43	108	138
	Max.	7.31	7.11	7.35	7.43	7.52	7.61	142	199
3.6.2b	Min.	7.07	6.94	7.02	7.13	7.18	7.29	61	129
	25%-ile	7.11	6.96	7.04	7.14	7.28	7.42	104	142
	Median	7.13	7.00	7.09	7.20	7.36	7.47	106#	145#
	75%-ile	7.17	7.05	7.25	7.25	7.54	7.52	122	152
	Max.	7.27	7.17	7.39	7.66	7.72	8.08	123	155

# denotes mean in place of median.
AN = Anaerobic zone; AE1 / AE2 = First / second aerobic zone respectively.

TABLE A2
Measured pilot plant results for ferric chloride dosing Periods 3.3.1 to 3.3.6
Results are averages with sample standard deviations in parentheses. N.D. = Not determined. Refer to nomenclature for definition of symbols.
The double horizontal line between experimental periods indicates a change in sludge age for operation of the units (refer to Table 3).

Period Unit	Days Fe dose, mg/ℓ Fe	Sti mgO/ℓ	Ste mgO/ℓ	Nti mgN/ℓ	Nte mgN/ℓ	Nae mgN/ℓ	No3e mgN/ℓ	Pti mgP/ℓ	Pte mgP/ℓ	P_{trem} mgP/ℓ	P/VSS mgP /gVSS	TSS mg/ℓ	VSS mg/ℓ	% VSS	DSVI mℓ/g	*f*Pt,a mgP/ℓ	*f*Pt,d mgP/ℓ	*f*Pt,b1 mgP/ℓ	*f*Pt,b2 mgP/ℓ
3.3.1 R1	62 days 10 mg/ℓ, AE1	442 (82)	21 (8)	31.3 (13.0)	2.86 (1.01)	0.22 (0.14)	7.14 (2.01)	49.85 (2.18)	22.73 (6.32)	27.12 (6.52)	203.4 (16.1)	4259 (611)	2238 (333)	52.6 (2.1)	65 (9)	95.8 (8.2)	50.8 (5.1)	34.2 (5.8)	24.5 (6.2)
3.3.1 R2	62 days 0 mg/ℓ	442 (82)	20 (4)	31.3 (13.0)	2.38 (0.77)	0.19 (0.10)	5.91 (2.13)	49.85 (2.18)	26.95 (5.38)	22.90 (5.94)	185.5 (7.69)	4121 (527)	2401 (299)	58.3 (1.4)	74 (9)	105.6 (8.9)	59.4 (6.4)	41.3 (6.3)	29.7 (5.6)
3.3.1(b) R1	31 days 10 mg/ℓ, AE1	398 (64)	20 (4)	27.7 (10.1)	2.36 (0.67)	0.27 (0.13)	6.76 (2.06)	48.86 (2.23)	21.63 (6.94)	27.23 (7.59)	213.7 (15.8)	4455 (324)	2273 (210)	51.0 (1.6)	73 (6)	93.5 (7.3)	49.7 (5.5)	34.6 (7.0)	24.5 (7.0)
3.3.1(b) R2	31 days 0 mg/ℓ	398 (64)	19 (4)	27.7 (10.1)	2.34 (0.81)	0.24 (0.09)	6.26 (1.96)	48.86 (2.23)	27.65 (5.24)	21.21 (6.18)	185.8 (7.7)	4296 (208)	2490 (79)	58.0 (1.7)	80 (4)	102.3 (8.4)	60.4 (6.6)	42.2 (6.0)	30.9 (5.0)
3.3.2 R1	34 days 20 mg/ℓ, AE1	407 (67)	19 (2)	31.3 (6.2)	2.34 (0.66)	1.46 (0.81)	6.11 (2.74)	48.80 (2.91)	15.05 (4.83)	33.76 (5.34)	271.1 (19.4)	5214 (427)	2357 (141)	45.3 (1.7)	75 (3)	104.1 (13.9)	51.2 (8.6)	27.1 (5.3)	16.7 (5.0)
3.3.2 R2	34 days 0 mg/ℓ	407 (67)	20 (3)	31.3 (6.2)	2.61 (1.02)	1.19 (0.61)	5.49 (2.48)	48.80 (2.91)	26.98 (5.03)	21.83 (5.57)	215.7 (12.4)	4595 (183)	2509 (68)	54.6 (1.4)	81 (5)	112.0 (10.3)	63.8 (12.5)	43.3 (8.1)	30.2 (5.8)
3.3.3 R1	27 days 10 mg/ℓ, AN	456 (57)	26 (11)	35.0 (7.1)	3.11 (1.09)	1.24 (0.23)	6.05 (1.39)	52.64 (3.84)	23.80 (4.26)	28.84 (5.95)	211.9 (13.0)	4547 (194)	2437 (83)	53.6 (2.0)	89 (12)	101.2 (10.6)	63.6 (9.3)	36.1 (7.8)	24.1 (6.6)
3.3.3 R2	27 days 0 mg/ℓ	456 (57)	21 (3)	35.0 (7.1)	2.64 (0.80)	1.16 (0.18)	6.27 (1.60)	52.64 (3.84)	28.34 (4.98)	24.30 (6.72)	192.7 (13.7)	4155 (216)	2424 (92)	58.4 (1.4)	104 (5)	107.2 (8.8)	61.0 (8.4)	40.8 (7.1)	29.7 (7.3)
3.3.4 R1	18 days 10 mg/ℓ, AN	461 (84)	22 (3)	33.5 (4.4)	3.38 (0.65)	1.74 (0.73)	6.39 (1.35)	50.61 (2.46)	18.88 (3.27)	31.73 (2.11)	220.0 (13.7)	3869 (433)	2009 (265)	51.9 (2.6)	82 (6)	105.7 (12.3)	56.6 (6.4)	31.9 (4.7)	19.4 (4.2)
3.3.4 R2	18 days 0 mg/ℓ	461 (84)	20 (3)	33.5 (4.4)	3.21 (1.21)	1.74 (0.90)	6.04 (1.29)	50.61 (2.46)	21.27 (5.19)	29.44 (4.19)	199.4 (11.9)	3562 (362)	1987 (196)	55.8 (1.9)	92 (4)	114.2 (10.8)	60.6 (6.8)	36.3 (6.9)	23.0 (7.1)
3.3.5 R1	21 days 20 mg/ℓ, AN	398 (61)	23 (7)	30.1 (5.7)	3.12 (0.83)	1.87 (0.45)	5.69 (1.63)	50.33 (3.40)	16.03 (4.35)	34.30 (5.22)	247.4 (36.3)	3275 (207)	1581 (142)	48.4 (5.1)	72 (5)	82.2 (4.6)	50.5 (5.5)	26.7 (5.6)	14.6 (5.3)
3.3.5 R2	21 days 0 mg/ℓ	398 (61)	21 (3)	30.1 (5.7)	2.75 (0.68)	1.66 (0.41)	6.59 (1.89)	50.33 (3.40)	25.29 (4.55)	25.04 (5.12)	207.5 (20.1)	2844 (253)	1546 (101)	54.5 (1.8)	79 (6)	95.6 (6.4)	57.6 (7.0)	37.2 (3.0)	24.4 (3.2)
3.3.6 R1	20 days 20 mg/ℓ, AE1	354 (94)	21 (5)	26.7 (3.5)	2.61 (0.99)	0.64 (0.47)	4.69 (0.71)	46.03 (2.55)	15.94 (4.08)	30.13 (5.55)	246.8 (9.6)	3205 (268)	1510 (146)	47.1 (1.3)	66 (3)	79.1 (14.5)	46.3 (6.0)	22.5 (6.2)	18.8 (5.0)
3.3.6 R2	20 days 0 mg/ℓ	354 (94)	21 (3)	26.7 (3.5)	2.48 (0.74)	0.64 (0.50)	6.16 (0.96)	46.03 (2.55)	21.64 (4.62)	24.42 (6.39)	224.6 (15.7)	2416 (192)	1319 (115)	54.6 (2.6)	84 (4)	93.9 (17.2)	36.7 (0.5)	28.7 (3.4)	22.8 (5.6)

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TABLE A3
Mass balances for ferric chloride dosing Periods 3.3.1 to 3.3.6
Results are averages with sample standard deviations in parentheses. Underlined results indicate estimates where spurious actual values were recorded. The double horizontal line between experimental periods indicates a change in sludge age for operation of the units (see Table 2).

Period Unit	Days Fe dose, mg/ℓ Fe	Flow Q, ℓ/d	VSS mg/ℓ	No3a mgN/ℓ	No3d mgN/ℓ	No3b2 mgN/ℓ	Nte mgN/ℓ	No3e mgN/ℓ	Nti mgN/ℓ	% N Bal.	Ot mgO/ℓ·h	Sti mgO/ℓ	Ste mgO/ℓ	% COD Bal.	P_{trem} mgP/ℓ	P/VSS mgP /gVSS	% P Bal.
3.3.1 R1	62 days 10 mg/ℓ, AE1	36.0	2238 (333)	0.06 (0.04)	3.34 (1.82)	6.68 (2.12)	2.86 (1.01)	7.14 (2.01)	31.3 (13.0)	96%	16.77 (1.80)	442 (82)	21 (8)	99%	27.12 (6.52)	203.4 (16.1)	75%
3.3.1 R2	62 days 0 mg/ℓ	36.2	2401 (299)	0.08 (0.05)	2.38 (1.82)	5.74 (2.14)	2.38 (0.77)	5.91 (2.13)	31.3 (13.0)	96%	17.98 (3.26)	442 (82)	20 (4)	103%	22.90 (5.94)	185.5 (7.69)	86%
3.3.1(b) R1	31 days 10 mg/ℓ, AE1	35.7	2273 (210)	0.08 (0.03)	3.75 (2.12)	6.48 (2.19)	2.36 (0.67)	6.76 (2.06)	27.7 (10.1)	96%	16.12 (1.44)	398 (64)	20 (4)	112%	27.23 (7.59)	213.7 (15.8)	80%
3.3.1(b) R2	31 days 0 mg/ℓ	35.9	2490 (79)	0.11 (0.05)	3.11 (1.74)	6.13 (1.96)	2.34 (0.81)	6.26 (1.96)	27.7 (10.1)	103%	16.23 (1.90)	398 (64)	19 (4)	114%	21.21 (6.18)	185.8 (7.7)	97%
3.3.2 R1	34 days 20 mg/ℓ, AE1	35.8	2357 (141)	0.11 (0.14)	1.10 (0.54)	5.15 (1.78)	2.34 (0.66)	6.11 (2.74)	31.3 (6.2)	109%	14.92 (1.64)	407 (67)	19 (2)	92%	33.76 (5.34)	271.1 (19.4)	85%
3.3.2 R2	34 days 0 mg/ℓ	36.0	2509 (68)	0.11 (0.14)	1.58 (2.70)	4.44 (2.72)	2.61 (1.02)	5.49 (2.48)	31.3 (6.2)	93%	18.16 (2.68)	407 (67)	20 (3)	102%	21.83 (5.57)	215.7 (12.4)	106%
3.3.3 R1	27 days 10 mg/ℓ, AN	36.0	2437 (83)	0.08 (0.03)	1.30 (0.72)	7.07 (0.66)	3.11 (1.09)	6.05 (1.39)	35.0 (7.1)	119%	14.48 (1.49)	456 (57)	26 (11)	91%	28.84 (5.95)	211.9 (13.0)	80%
3.3.3 R2	27 days 0 mg/ℓ	35.8	2424 (92)	0.15 (0.09)	2.78 (1.45)	6.94 (0.80)	2.64 (0.80)	6.27 (1.60)	35.0 (7.1)	96%	15.54 (2.66)	456 (57)	21 (3)	95%	24.30 (6.72)	192.7 (13.7)	86%
3.3.4 R1	18 days 10 mg/ℓ, AN	36.0	2009 (265)	0.07 (0.04)	1.56 (0.73)	6.18 (1.49)	3.38 (0.65)	6.39 (1.35)	33.5? <u>41.9</u>	133% 106%	14.03 (1.02)	461 (84)	22 (3)	98%	31.73 (2.11)	220.0 (13.7)	125%
3.3.4 R2	18 days 0 mg/ℓ	36.2	1987 (196)	0.10 (0.01)	1.86 (0.69)	5.98 (1.35)	3.21 (1.21)	6.04 (1.29)	33.5? <u>41.9</u>	124% 99%	13.89 (0.96)	461 (84)	20 (3)	98%	29.44 (4.19)	199.4 (11.9)	119%
3.3.5 R1	21 days 20 mg/ℓ, AN	36.4	1581 (142)	0.05 (0.03)	0.80 (0.46)	6.80 (1.39)	3.12 (0.83)	5.69 (1.63)	30.1? <u>37.6</u>	143% 122%	12.44 (1.75)	398 (61)	23 (7)	91%	34.30 (5.22)	247.4 (36.3)	100%
3.3.5 R2	21 days 0 mg/ℓ	36.1	1546 (101)	0.07 (0.02)	2.48 (0.94)	7.44 (0.95)	2.75 (0.68)	6.59 (1.89)	30.1? <u>37.6</u>	134% 107%	12.83 (1.24)	398 (61)	21 (3)	92%	25.04 (5.12)	207.5 (20.1)	114%
3.3.6 R1	20 days 20 mg/ℓ, AE1	36.3	1510 (146)	0.07 (0.03)	1.18 (1.05)	4.92 (0.53)	2.61 (0.99)	4.69 (0.71)	26.7? <u>33.4</u>	129% 103%	11.76 (2.57)	354 (94)	21 (5)	102%	29.27 (6.64)	246.8 (9.6)	112%
3.3.6 R2	20 days 0 mg/ℓ	36.6	1319 (115)	0.05 (0.02)	4.69 ? <u>2.20</u>	5.94 (0.86)	2.48 (0.74)	6.16 (0.96)	26.7? <u>33.4</u>	61% 99%	14.72 (1.69)	354 (94)	21 (3)	98%	24.05 (6.66)	224.6 (15.7)	108%
								Mean (excl. Period 3.3.1):		104%		Mean (excl. Period 3.3.1):		99%	Mean (excl. Period 3.3.1):		101%
									S.D.:	9%			S.D.:	7%		S.D.:	16%

TABLE A4a

Measured pilot plant results for ferric chloride dosing Periods 3.6.1 to 3.6.2 (a & b). Results are averages with sample standard deviations in parentheses. The double horizontal line between experimental periods indicates a change in influent alkalinity or phosphorus for the units (see Table 1).

Period Unit	Sti mgO/ℓ	Ste mgO/ℓ	Nti mgN/ℓ	Nte mgN/ℓ	Nae mgN/ℓ	No3e mgN/ℓ	Pti mgP/ℓ	Pte mgP/ℓ	P_{trem} mgP/ℓ /gVSS	P/VSS mgP	TSS mg/ℓ	VSS mg/ℓ	% VSS	DSVI mℓ/g	*f*Pt,a mgP/ℓ	*f*Pt,d mgP/ℓ	*f*Pt,b1 mgP/ℓ	*f*Pt,b2 mgP/ℓ
3.6.1 R1	403 (105)	52 (23)	31.1 (6.2)	2.4 (1.0)	1.04 (0.80)	7.08 (2.61)	10.45 (2.15)	0.45 (0.37)	9.85 (2.05)	80.10 (5.24)	1933 (133)	1291 (110)	66.8 (1.8)	64 (7)	25.38 (5.13)	7.99 (2.18)	1.27 (0.62)	0.41 (0.27)
3.6.1 R2	403 (105)	58 (20)	31.1 (6.2)	2.2 (0.6)	0.50 (0.50)	6.24 (2.60)	10.45 (2.15)	0.43 (0.43)	10.01 (2.00)	91.14 (5.68)	1662 (122)	1218 (89)	73.3 (2.0)	104 (26)	40.12 (7.35)	15.50 (3.54)	2.97 (2.09)	0.37 (0.23)
3.6.2a R1	427 (82)	44 (22)	31.8 (4.6)	2.1 (0.3)	1.13 (0.84)	5.33 (1.39)	10.46 (3.02)	0.53 (0.45)	9.93 (2.92)	89.65 (11.53)	1849 (220)	1223 (160)	66.0 (1.7)	72 (10)	25.73 (6.32)	8.44 (2.72)	1.51 (0.79)	0.41 (0.26)
3.6.2a R2	427 (82)	41 (11)	31.8 (4.6)	2.1 (0.3)	0.59 (0.52)	4.74 (1.42)	10.46 (3.02)	0.62 (0.94)	9.84 (3.25)	96.91 (9.61)	1638 (192)	1186 (121)	72.6 (2.4)	130 (10)	40.52 (8.19)	14.76 (3.04)	2.71 (1.99)	0.63 (0.77)
3.6.2b R1	324 (52)	31 (12)	25.92 (3.47)	2.0 (-)	0.66 (0.52)	4.00 (0.66)	25.85 (6.82)	10.42 (5.01)	15.43 (5.97)	123.98 (24.16)	1633 (73)	1031 (34)	63.1 (2.4)	79 (2)	38.27 (13.76)	18.52 (7.53)	13.17 (6.24)	9.35 (4.60)
3.6.2b R2	324 (52)	34 (15)	25.92 (3.47)	2.0 (-)	0.46 (0.43)	4.29 (0.70)	25.85 (6.82)	11.15 (6.16)	14.70 (7.07)	130.89 (23.24)	1328 (58)	961 (25)	72.5 (2.4)	118 (4)	53.36 (5.88)	23.40 (8.19)	15.05 (6.97)	9.42 (5.25)

f = filtered; a = anaerobic; d = anoxic; b1 = 1st aerobic; b2 = 2nd aerobic reactors of 3-stage Phoredox system (see Fig. 1, Part 3).

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TABLE A4b
Additional pilot plant results measured for ferric chloride dosing periods 3.6.1 to 3.6.2 (a & b). Results are averages with sample standard deviations in parentheses. Refer to Mamais et al. (1993) for S_{bsi} method. The double horizontal line between experimental periods indicates a change in influent alkalinity or phosphorus for the units (see Table 1).

Period Unit	Sbsi+Susi mgO/ℓ Mamais	Sbsi mgO/ℓ Mamais	Nai mgN/ℓ	PO_4i mgP/ℓ	*f*PO_4, a mgP/ℓ	*f*PO_4, d mgP/ℓ	*f*PO_4, b1 mgP/ℓ	*f*PO_4, b2 mgP/ℓ	PO_4e mgP/ℓ
3.6.1 R1	230 (88)	172 (-)	21.16 (3.80)	7.56 (1.49)	22.50 (4.37)	7.04 (1.80)	1.01 (0.50)	0.31 (0.25)	0.24 (0.15)
3.6.1 R2	230 (88)	172 (-)	21.16 (3.80)	7.56 (1.49)	37.26 (7.30)	14.31 (3.22)	2.27 (1.04)	0.34 (0.24)	0.21 (0.25)
3.6.2a R1	219 (55)	178 (-)	20.15 (3.14)	7.84 (2.54)	23.19 (5.65)	7.53 (2.43)	1.29 (0.67)	0.32 (0.24)	0.35 (0.34)
3.6.2a R2	219 (55)	178 (-)	20.15 (3.14)	7.84 (2.54)	39.11 (6.82)	13.35 (2.86)	2.44 (1.95)	0.52 (0.75)	0.44 (0.85)
3.6.2b R1	174 (40)	140 (-)	17.22 (1.18)	22.52 (6.48)	33.90 (10.66)	17.11 (6.82)	11.64 (5.28)	8.33 (3.85)	8.79 (3.86)
3.6.2b R2	174 (40)	140 (-)	17.22 (1.18)	22.52 (6.48)	45.73 (11.96)	21.89 (7.18)	13.22 (5.93)	8.94 (4.71)	9.23 (4.93)

TABLE A5
Mass balances for ferric chloride dosing periods 3.6.1 and 3.6.2 (a & b).
Results are averages with sample standard deviations in parentheses.

Period Unit	Flow Q, ℓ/d	VSS mg/ℓ	No3a mgN/ℓ	No3d mgN/ℓ	No3b2 mgN/ℓ	Nte mgN/ℓ	No3e mgN/ℓ	Nti mgN/ℓ	% N Bal.	Ot mgO/ℓ.h	Sti mgO/ℓ gVSS	Ste mgO/ℓ	% COD Bal.	P_{trem} mgP/ℓ	P/VSS mgP/	% P Bal.
3.6.1 R1 45 days 10 mg/ℓ Fe, AE1	35.8 (1.0)	1291 (110)	0.25 -	3.60 (1.72)	6.94 (2.63)	7.20 (2.83)	7.08 (2.61)	31.1 (6.2)	102	13.13 (1.61)	403 (105)	52 (23)	99	9.85 (2.05)	80.10 (5.24)	94
3.6.1 R2 Control	35.8 (0.8)	1218 (89)	0.25 -	6.94 (2.63)	6.40 (2.33)	6.68 (2.74)	7.56 (1.49)	31.1 (6.2)	102	14.23 (1.33)	403 (105)	58 (20)	100	10.01 (2.00)	91.14 (5.68)	99
3.6.2a R1 64 days 10 mg/ℓ Fe, AE1	35.9 (1.9)	1223 (160)	0.25 -	2.83 (0.71)	5.43 (1.38)	2.06 (0.26)	5.33 (1.39)	31.77 (4.56)	81	11.36 (1.57)	415 (88)	44 (22)	95	9.93 (2.92)	89.65 (11.53)	98
3.6.2a R2 Control	35.4 (2.0)	1186 (121)	0.25 -	2.31 (0.77)	4.70 (1.24)	2.09 (0.32)	4.74 (1.42)	31.77 (4.56)	78	12.87 (2.35)	415 (88)	41 (11)	97	9.84 (3.25)	96.91 (9.61)	106
3.6.2b R1 12 days 10 mg/ℓ Fe, AE 1	Mass balances not attempted - short experimental period (12 d) and systems not in steady state, due to addition of influent P															
3.6.2b R2 Control	Mass balances not attempted - short experimental period (12 d) and systems not in steady state, due to addition of influent P															