The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological excess phosphate removal
Part 3: Experimental periods using alum

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Abstract

An investigation was conducted into the effect of simultaneous alum dosing on biological phosphorus (P) removal in an activated sludge system at pilot scale. Two continuous flow (36 ℓ/d) activated sludge pilot plants were used to develop "semi-enhanced" biological excess phosphorus removal (BEPR) organism cultures of activated sludge by means of acetate supplementation of the feed. BEPR was strongly exhibited in these systems. One was used as a test system (to which alum was dosed), while the other served as control (no chemical addition). Additional removal due to chemical precipitation was measured as the difference in system P removal between the two systems. 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 in the test system. Phosphorus fractionation of the mixed liquor suspended solids also served as an indicator of the respective biological and chemical mechanisms. Evidence was found that the BEPR mechanism is partially inhibited in the presence of simultaneous alum addition, even in the absence of effluent phosphate limitation. However, the degree of inhibition was relatively low, ranging 15 to 25% (approximately) for alum doses in the range ca. 5 to 9 mg/ℓ as Al (50 to 100 mg/ℓ as dry alum), at a system P removal of 20 to 30 mgP/ℓ in the control. Alum dosing in this range was sufficient to produce additional P removal of the order of 3 to 7 mgP/ℓ over periods of one to three sludge ages per experimental period. Sustained operation of the BEPR mechanism in the presence of alum was possible over a continuous period of 7 sludge ages.

Nomenclature

Δ	Delta, meaning "difference in" or "change in" (e.g. $\Delta M,P_{rem}$ - see also below)
AE1 or 2	Aerobic zone or reactor
Al~P~O	Aluminium phosphate oxide precipitate (theoretical) after ashing of aluminium hydroxy-phosphate
Al~P~OH	Aluminium hydroxy-phosphate
Alk.	Alkalinity (unless otherwise stated: bicarbonate alkalinity)
AN	Anaerobic zone or reactor
AX	Anoxic zone or reactor
BEPR	Biological excess phosphorus removal
COD	Chemical oxygen demand
DSVI	Dilute sludge volume index
$fP_{t,a}$	*Filtered* total P in the anaerobic reactor
ISS	Inorganic suspended solids
M,P_{rem}	Mass of phosphate removed
M,P_{rel}	Mass of phosphate released (in anaerobic zone)
orthoP	Orthophosphate
PCA	Perchloric acid (fractionation studies)
polyP	Polyphosphate
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	Return sludge flow rate (clarifier underflow)
rem	Removal/ removed
RES	Residue (in fractionation studies)
SD	Sample standard deviation
SUP	Supernatant (in fractionation studies)
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
VSS	Volatile suspended solids

Introduction

Aluminium sulphate (alum) is commonly used as a simultaneous chemical precipitant for phosphorus (P) removal in activated sludge systems. As discussed in **Part 1** of this series of papers (De Haas et al., 2000a), chemical addition is frequently required to supplement P removal in modified activated sludge systems designed to remove P biologically where such systems are unable to achieve the required effluent P concentration by biological means alone. However, a degree of uncertainty surrounds the question of possible inhibition of the biological P removal processes due to the simultaneous addition of chemical precipitants. Due to the relevance of the research topic to Umgeni Water and its operation of Darvill Wastewater Works (WWW) in Pietermaritzburg (South Africa), a pilot-plant facility was established at this works with a view to testing the effect of simultaneous chemical addition on excess biological P removal in activated sludge systems.

The initial phase of the research using pilot plants was aimed at dosing aluminium sulphate (alum) as simultaneous precipitant. At Darvill WWW, alum had been used as simultaneous precipitant with fair success over a period of approximately 18 months prior to the commencement of this study. The biological P removal mechanism was apparently still operative in the full-scale plant at Darvill WWW in the presence of alum dosing (as evidenced by P release in the anaerobic zone, for example). However, the absence of a

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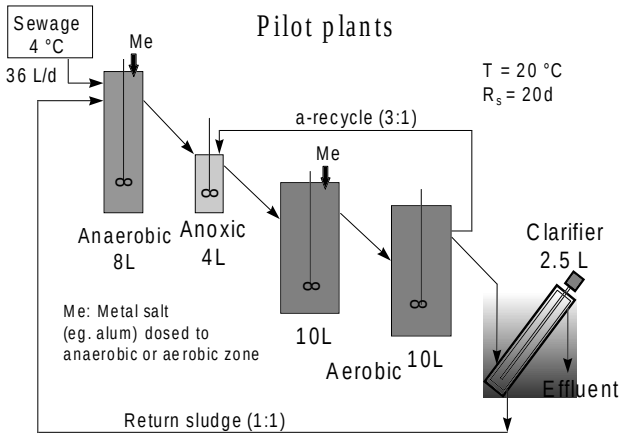


Figure 1
Schematic layout of pilot-plant configuration (three-stage Phoredox process). Alternative metal salt (Me) dosing points to anaerobic or aerobic zone indicated.

control reactor made it impossible to determine the extent to which the chemical mechanism inhibited or "competed with" the biological mechanism.

The objective at the outset of this study was to set up two parallel pilot plants which strongly exhibited the BEPR phenomenon, in order to observe as clearly as possible any effects which simultaneous chemical precipitants (e.g. alum) may have on the biological mechanism. After an initial phase in which so-called "enhanced cultures" of BEPR organisms strongly exhibiting P removal had been established in both pilot plants (Wentzel et al., 1988), chemical precipitant would be dosed into only one unit (named the test unit or R1), while the other served as the control (R2). The effect of chemical dosing to either the anaerobic or aerobic zone could then be studied over several experimental periods. Phosphate was always added to the influent of the pilot plants to ensure that phosphate was never limiting. On this basis P removal potential could to be measured and compared between the test and control units.

Materials and methods

Pilot plant set-up

A modified, insulated shipping container (6 m long) was used as an outside laboratory for housing the pilot plants. In view of the space constraints, laboratory-scale units (manufactured by UCT Dept. of Civil Engineering Workshop) were used. A facility for withdrawing sewage from the full-scale plant for feeding to the pilot plants was provided. This was accomplished using a small submersible pump (ca. 50 ℓ/min) suspended in a sump through which settled sewage flowed continuously into the full-scale activated sludge plant at Darvill WWW. The submersible pump was used to fill a refrigerated intermediate storage tank (500 ℓ, refrigerated at 2 to 4°C) with settled sewage once or twice per week.

Two identical pilot-plant units (R1 and R2) were set up with a three-stage Phoredox configuration and operated at 20 (± 2)°C. A schematic layout of the pilot plants is given in Fig. 1. The reactor configuration was as follows: anaerobic (AN) zone (8 ℓ); anoxic (AX) zone (4 ℓ); first aerobic (AE1) zone (10 ℓ); second aerobic (AE2) zone (10 ℓ); clarifier (2.5 ℓ); target influent flow rate (Q_i) = 32 or 36 ℓ/d (see **Results and Discussion**) fed to the AN zone; s-recycle ratio from clarifier to AN zone = 1:1 and a-recycle ratio from AE2 to AX zone = 3:1, both with respect to influent flow.

Batches of influent (160 ℓ) were prepared every second day, taken from settled sewage stored in the 500 ℓ cold storage tank (see above). The 160 ℓ tank was made of stainless steel and equipped with a refrigerated jacket which allowed the contents to be kept at 4°C. This tank was the source of feed common to both R1 and R2 for two days, following which it was cleaned and refilled.

Sludge wasting was achieved by daily withdrawal of the appropriate volume of mixed liquor (1.6 ℓ) from the second aerobic reactor (AE2) in order to maintain a sludge age of 20 d. Oxygen uptake rate (OUR) was measured in the AE2 zone by means of OUR meters (Randall et al., 1991). The air supply to the aerobic zones in each unit was controlled such that the aquarium air pumps switched on at a dissolved oxygen (DO) concentration of 3.0 mg/ℓ and switched off at a DO concentration of 5.0 mg/ℓ.

Pilot-plant operation and enhanced culture development

Starting with a seed of activated sludge, it is possible to develop so-called enhanced cultures of BEPR organisms exhibiting the BEPR mechanism very strongly. Increased supplementation with ideal substrate (e.g. acetate) and the addition of macronutrients (Mg^{2+} and K^+ ions) and micronutrients (e.g. trace metals) is required, reaching the point where acetate serves as the sole carbon source (Wentzel et al., 1988). The objective of this project was to develop semi-enhanced cultures such that the feed would always contain a sewage component, thereby obviating the need for micronutrient addition. However, the sewage would be supplemented with sodium acetate and macronutrients (Mg and K) to ensure that BEPR was always strongly exhibited. From the work of Wentzel et al. (1988) it was foreseen that pH control would become increasingly critical with increasing acetate dose. The reason for this is that when feeding sodium acetate, the BEPR mechanism causes an increase in pH in the aerobic reactors due to utilisation of stored carbon sources originating mainly from the acetate fed (Wentzel et al., 1986; Gerber et al., 1987; Wentzel et al., 1988); the increase in pH necessitates acid dosing to keep the pH below 8.0 such that chemical phosphate precipitation (notably calcium and magnesium salts) is discouraged. Accordingly, it was decided to develop semi-enhanced cultures only up to the point of supplementing a maximum of 250 mg/ℓ COD as acetate in order to avoid as far as possible the precipitation of calcium or magnesium phosphate(s). A further objective was to attain a constant influent COD of 500 mg/ℓ in an attempt to reach steady-state in the pilot plants. In practice, the 500 mg/ℓ influent COD target proved difficult to achieve since the Darvill settled sewage was relatively weak, averaging around 250 to 350 mg/ℓ COD under dry weather conditions and <100 to 250 mg/ℓ COD under wet weather conditions. *[The city of Pietermaritzburg, which is the catchment for Darvill WWW, has a history of severe stormwater and groundwater intrusion of the sewer network (Meiring and Barnard, 1990; WLPU-WMB, 1993)]*. Since it may be expected that the variable addition of another synthetic substrate (e.g. peptone or starch) to make up the deficit in influent COD would exert a further strong influence on the BEPR mechanism, it was decided to accept a lower average (and more variable) influent COD concentration with sodium acetate as the sole organic supplement.

Enhanced (or semi-enhanced) cultures were developed three times in this study (Tables 1 and 2). The first led to Period 3.1.6, which had to be abandoned (see **Results and Discussion**). A second culture was then developed (Period 3.2.1). Between Period 3.2.6 and 3.2.7 it was necessary to redevelop enhanced cultures for practical reasons, arising from the need to completely relocate the

TABLE 1
Sewage supplement composition by experimental period
(Refer to Table 2 for relevant alum and acid dose)

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 $CaCO_3$
3.1.1 (No Alum)	23/2/94 to 15/3/94	20	50	10	2.8	25	0
3.1.2 (No Alum)	16/3/94 to 6/4/94	22	100	20	5.6 till 31/3/96 8.4 thereafter	50	0
3.1.3 (No Alum)	7/4/94 to 30/4/94	24	150	30	12.6	75	0
3.1.4 (No Alum)	1/5/94 to 16/5/94	16	200	40	16.8	100	0
3.1.5 (No Alum)	17/5/94 to 31/5/94	15	250	40	21.0	100	0
3.1.6 (Alum)	1/6/94 to 20/7/94	50	250	40	21.0	100	0
New enhanced culture developed	27/7/94 to 19/8/94	24	50 then 100 then 150	20 then 30 then 40	12.6	50 then 75 then 100	50
3.2.1 (No alum)	19/8/94 to 31/8/94	13	150	40	12.6	100	50
3.2.2 (Alum)	1/9/94 to 26/9/94	26	150	40	12.6	100	50
3.2.3 (Alum)	27/9/94 to 7/11/94	40	150	40	12.6	100	100
3.2.4 (Alum)	8/11/94 to 26/12/94	49	150	40	12.6	100	100
3.2.5 (Alum)	27/12/94 to 9/1/95	14	150	40	12.6	100	150
3.2.6 (Alum)	10/1/95 to 23/1/95	14	150	40	12.6	100	150
New enhanced culture developed (No alum)	25/1/95 to 19/2/95	26	50 then 100 then 150	20 then 30 then 40	12.6	50 then 75 then 100	150
3.2.7 (Alum)	20/2/95 to 22/3/95	31	150	40	12.6	100	150
3.2.8a (Alum)	23/3/95 to 13/4/95	22	150	40	12.6	100	0
3.2.8b (Alum)	16/4/95 to 25/4/95	10	150	40	12.6	100	0

pilot-plant facility within Darvill WWW due to construction activity on the full-scale plant at that time.

Table 1 gives the composition of sewage supplements for the experimental periods relevant to this chapter. Each sewage batch (160 ℓ) was augmented with the following constituents (refer to Table 1):

- sodium acetate (typically 150 mg/ℓ as COD);
- orthophosphate (typically 40 mgP/ℓ as K_2HPO_4);
- magnesium chloride (84 mg Mg per g COD as acetate added; typically 12.6 mg Mg/ℓ);
- sodium bicarbonate for alkalinity (typically a supplement of 100 mg/ℓ as $CaCO_3$) in certain experimental periods.

The general pilot-plant maintenance and operational procedures as set out in detail by Burke et al. (1986) and Clayton et al. (1989) were followed.

The reactor interior surfaces were brushed every day. Occasional problems were experienced with the proliferation of protozoa or "worms" in the reactors, causing blockages of the tubing interconnecting the reactors. *[Detailed investigation of the causes of this was not undertaken. It appears that the attachment of organic material from either the sewage or biomass to the walls of the reactors provided an ideal habitat for these organisms. Two organisms were identified as contributing to the problem. The first was the protozoan* Vorticella*, with stalks bound in dense masses sometimes called "rosettes" and appearing to the naked eye as whitish lumps in the reactors. The other was larvae of* Psychoda *flies, which were common at Darvill WWW, and were visible to the naked eye as small red worms. Other fly larvae were also occasionally found].* During these periods the problem could be kept under control by sieving the contents of the AN and AX zones on a fairly regular basis, as well as a periodic clean out of all reactors. The mixed liquor was always recovered after sieving and returned to the reactors after the latter had been washed.

Pump tubing lines were cleaned daily by means of squeezing or brushing. Soft silicone tubing proved to be the easiest to keep clean.

Alum dosing

As a point of departure, it was assumed that a molar ratio of 0.5 mol P_{trem}/ mol Al_{dosed} would be achievable (Wiechers, 1987). Accepting this ratio, a dose of 6.2 mmol Aℓ/d and 12.4 mmol Aℓ/d at a influent

TABLE 2
Experimental periods of alum and acid dosing to UCT pilot plants (Refer also to Table 1 for feed composition details)

Period name	Date range	No. of days	Zone dosed with alum/ acid	Alum dose to R1 (test) reactor (mmol/d as Al)	Acid (HCl) dose (mmol/d)	Target influent flow rate (ℓ/d)
Enhanced culture development Periods 3.1.1 to 3.1.5 50 to 250 Acetate, No alum	23/2/94 to 31/5/94	97	-	0	0 to 120	32
3.1.6 : 250 Acetate, Low alum	1/6/94 to 20/7/94	50	AE1	6.2	60 to 120 (R1 avg. = 90) (R2 avg. = 100)	32
New enhanced culture developed 3.2.1 : 150 Acetate, No alum	27/7/94 to 31/8/94	13	-	0	0	34
3.2.2 : 150 Acetate, Low Alum	1/9/94 to 26/9/94	26	AE1	6.2	0	34
3.2.3 : 150 Acetate, Low Alum	27/9/94 to 7/11/94	40	AE1	6.2	10	36
3.2.4 : 150 Acetate, Low Alum	8/11/94 to 26/12/94	49	AN	6.2	10	36
3.2.5 : 150 Acetate, High Alum	27/12/94 to 9/1/95	14	AN	12.4	10	36
3.2.6 : 150 Acetate, High Alum	10/1/95 to 23/1/95	14	AE1	12.4	10	36
New enhanced culture developed 150 Acetate, No alum	25/1/95 to 19/2/95	26	-	0	0	36
3.2.7 : 150 Acetate, High Alum	20/2/95 to 22/3/95	31	AE1	12.4	10	36
3.2.8a : 150 Acetate, High Alum	23/3/95 to 13/4/95	22	AE1	12.4	10	36
3.2.8b : 150 Acetate, High Alum	16/4/95 to 25/4/95	10	AE1	12.4	10	36

sewage flow rate of 32 ℓ/d corresponds to a dose of 5.2 and 10.4 mg/ℓ as Al respectively (or 4.7 and 9.3 mg/ℓ as Al respectively at an influent flow rate of 36 ℓ/d). This is sufficient to give additional P removal of ca. 3 and 6 mgP/ℓ respectively at an influent flow rate of 32 ℓ/d (or 2.7 and 5.3 mgP/ℓ at a flow rate of 36 ℓ/d). On the basis of full-scale operating experience at Darvill WWW, this appeared to be a reasonable target for "low" and "high" alum doses. A dilute solution of alum ($Al_2(SO_4)_3.14H_2O$, supplied by *Minamet*, Durban) in tap water was prepared to meet these "low" and "high" doses and fed into R1 AN or AE1 zone continuously 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 dilute alum solutions. For this reason, a minimum of 10 mmol/d of HCl (equivalent to approximately 15 mg/ℓ as $CaCO_3$) was added to the dilute alum solution dosed to R1. The same amount of acid was fed in tap water only to R2, also at a rate of 500 mℓ/d.

Table 2 gives alum and acid doses used according to experimental period.

Parameters measured

All parameters measured were in accordance with *Standard Methods* (1985) or methods described in Part 2 of this series of papers (De Haas et al., 2000b). The only exceptions were: OUR, which was measured according to Randall et al. (1991); DSVI, which was measured according to Ekama and Marais (1984); and COD, which was measured by the open reflux digestion and manual titration method given in *Standard Methods* (1985) for effluent samples, and by a microwave digestion method followed by automated potentiometric titration (Slatter and Alborough, 1990) for influent samples. *[It was found that the open reflux method gave poor recoveries (56 to 66%) of sodium acetate COD, both from pure solutions and in admixture with settled sewage, possibly due to the reflux condenser length (50 cm) being inadequate. Better recoveries (90 to 105%) were obtained by the microwave method which uses closed reflux in Teflon pressure vessels]*.

Chemical fractionation of sludge samples

A literature review of fractionation methods applied to phosphorus compounds in activated sludge was presented in **Part 1** of this series of papers (De Haas et al., 2000a). Fractionation and P release batch tests were carried out according to the procedure described in **Part 2** of this series of papers (De Haas et al., 2000b).

Results and discussion

First alum dosing period (with high acid dose)

From Tables 1 and 2, it may be seen that during Period 3.1.6 (50 days), alum was dosed into R1 (6.2 mmol/d as Al into AE1), while R2 served as the control. The acetate dose was kept constant at 250

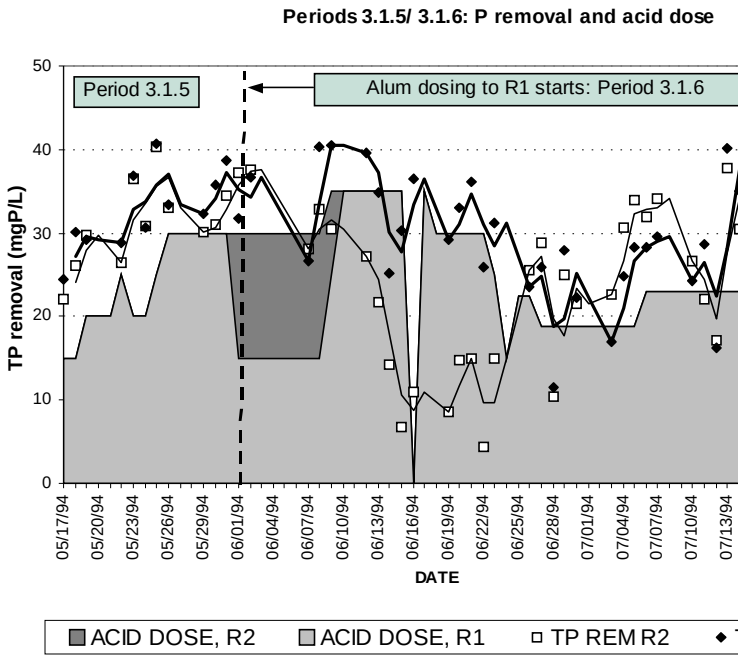


Figure 2
TP removal and acid dose data for pilot plants in experimental period 3.1.6 with low alum dose to R1, 250 mg/ℓ COD acetate feed and high acid dose to both. Acid dose was equal in R1 & R2 excepting period 94/06/01 to 94/06/10. Lines are two-point moving averages.

mg/ℓ (as COD) and acid was dosed in a similar manner into both systems. Initially, as the enhanced culture was developed, the acid dose was increased in an attempt to keep the pH in the aerobic reactors below 7.8 so as to minimise "background" chemical precipitation of phosphorus. Dilute hydrochloric acid (10 to 140 mmol/d HCl) was dosed to the first aerobic zone of both units, or incorporated with the solution of dilute alum in the case of R1 (see **Materials and Methods** and Table 2).

It was found that the pilot plants developed operational problems during Period 3.1.6. Firstly, P removal was very unstable. The two units had shown similar P removals in Period 3.1.5 (Fig. 2). However, shortly after the increase in acid dose (8/6/94), P removal deteriorated, first and most markedly in R2 (control), but subsequently also in R1. P removal appeared to recover to some extent later in the experimental period when the acid dose was reduced. Secondly, operation of the units became very difficult due to settling problems associated with the emergence of a pin-floc sludge. This was not evident from the DSVI results, but from visual observations the settling rate of the sludge was reduced, at first in R1, and progressively also in R2 (control). In association with the settling problems, the effluents tended to be turbid, presumably due to large numbers of free bacteria in the effluent. By the third week of July 1994, the units were deemed inoperable.

No clear evaluation of the causes of the operational problems during this early part of the experimentation could be made from the available data. The tendency toward pin floc formation (or poor flocculation) in both units may have been related to the relatively long sludge age and high influent soluble substrate (acetate) concentration. A comparison of the effluent soluble P and total P data showed a difference of 2.2 (±1.2) mgP/ℓ for R1 on a mean (± SD) basis, and 0.8 (± 0.4) for R2. Considering that the total P content of the mixed liquor suspended solids was close to 110 (±10) mgP/g MLSS for both units in this period, it may be concluded that an elevated effluent suspended solids content due to poor flocculation alone did not account for the deterioration in P removal by ~20 mgP/ℓ observed (Fig. 2).

It was tentatively concluded that a combination of high acid dose (or relatively low system alkalinity) and other operating conditions (e.g. high acetate concentration) had led to the operational problems experienced during Period 3.1.6. Accordingly, it was decided to restart the experiments, feeding less acetate and taking more care with pH control.

Second alum dosing period

Following the operational difficulties during the first alum dosing period, a second attempt was made to achieve steady-state operation of the pilot plants in the presence of sustained simultaneous alum addition. The primary objective was to test whether significant and inevitable deterioration of the BEPR mechanism would occur in the unit dosed with alum compared to the control. A secondary objective was to attempt to test the hypothesis that pin floc sludge settling problems and BEPR deterioration in the first alum dosing period were associated with the high acid dose administered during that period. Accordingly, in the second alum dosing period the following operational strategy was adopted (refer also to Tables 1 and 3):

- New "semi-enhanced" cultures were developed, starting with 50 mg/ℓ influent as acetate COD.
- The maximum acetate feed concentration was 150 mg/ℓ influent as COD (reduced from 250 mg/ℓ).
- Alkalinity supplement was added to the sewage in the form of sodium bicarbonate in the range 50 to 150 (usually 100) mg/ℓ as $CaCO_3$, based on influent.
- Acid dose was reduced to a minimum for preventing hydroxide coagulation in alum feed (10 mmol/d as HCl or approx. 15 mg/ℓ as $CaCO_3$, based on influent).

It was found that this strategy was successful in allowing stable operation of the pilot plants without the emergence of pin floc settling problems. The pH in the aerobic reactors never rose above pH 7.9 (Table A1, Appendix A), thereby limiting formation of phosphate precipitates involving calcium and magnesium ions.

Mass balances for COD, N and P (second alum dosing period)

The mass balance data in Table A3 (Appendix A) show considerable variation. One of the root causes for this variation was a deficiency in the experimental set-up, namely, that the influent COD and TKN concentrations varied considerably. This problem stemmed from the fact that the source sewage at Darvill WWW usually was so dilute that even with acetate addition (theoretical 150 mg/ℓ as COD), the influent COD to the pilot plants seldom exceeded 500 mg/ℓ (the original target concentration). Since it was not considered desirable (from the point of view of affecting the biological nutrient removal mechanisms) to further dilute the sewage, nor to add any other artificial substrates to maintain a constant COD or TKN, it was decided to accept the variations arising from the experimental set-up. During the periods under review (Periods 3.2.2 to 3.2.8b), a further factor affecting the N mass balances was problems experienced with the method used for TKN analysis. *[In the TKN method used, the time under sulphuric acid digestion was found to be critical. The method used required digestion at 380°C for 2½ h after the water has been evaporated off over approximately 1 h at 180°C. It was found that accurate control of the heating block temperature was difficult to achieve in practice and required considerable trial-and-error. A general observation was that if the initial heating period was too long (or too rapid, at temperatures exceeding 180°C), then at the end of the total digestion time, the samples often crystallised. Difficulty was then experienced in re-dissolving the precipitate at room temperature and low recovery of nitrogen sometimes occurred in quality control checks. On the other hand, if the digestion period was made too short, low TKN results were reported, probably due to incomplete digestion. The ideal digestion time and heat setting on the block were found to be those which produced a clear syrup after digestion for 2 h (following the initial hour for water evaporation) and cooling to room temperature. If crystallisation occurred, the sample was discarded and the analysis repeated].*

Despite the above-mentioned difficulties, most of the mass balance results ranged around 100 (±20) %, which suggested that the results were acceptable for further interpretation and that the pilot plants were operating fairly close to steady-state during experimental periods 3.2.2 to 3.2.8b.

P mass balance around the anaerobic reactor

Accepting that $Q_i = Q_s$ (return sludge recycle ratio = 1:1), from mass balance considerations around the anaerobic reactor it can be shown that:

$$M,P_{rel} = [(Q_i + Q_s).\, fP_{t,a}] - [Q_i.P_{ti} + Q_s.P_{te}] \qquad (3.1)$$

where $M(P_{rel})$ is the mass of phosphate released to the (filtered) supernatant in the anaerobic zone.

Using Eq. (3.1) and the measured data for P_{ti}, P_{te} and $fP_{t,a}$, the mass of P release in the anaerobic reactor of the test unit (R1, alum dosed) can be compared to that of the control (R2) and expressed on a percentage basis. The results are presented in Table 3.

The data in Table 3 suggest that initially alum dosing had no discernible effect on the biological P removal mechanism, as measured by P release in the anaerobic zone. This was evident for two periods (3.2.2 and 3.2.7) both of which followed on from the development of new semi-enhanced cultures. For these periods, P release in R1 was similar to R2, with relatively large variance in the data and the 95% confidence interval of the mean for $M,P_{rel,R1}/M,P_{rel,\ R2}$ spanning 100%. With time, the variance in the data became less, probably because the systems moved closer to steady state. In Period 3.2.3, the extent of inhibition due to alum dosing was slight or negligible, considering the 95% confidence interval of the mean (Table 3). In Period 3.2.4, apparent inhibition was discernible and this continued into Period 3.2.5. Significantly, however, in both these periods alum was dosed to the anaerobic zone, which probably resulted in precipitation of a portion of the released phosphate. In Period 3.2.6, with the same alum dose as Period 3.2.5 but dosed to the aerobic zone, less inhibition (10% ±3) was apparent from the P release data (Table 3). Similarly, in Period 3.2.8a with alum dosed to the aerobic zone (without influent alkalinity supplement), inhibition was slight but increasing later in Period 3.2.8b (17% ± 4).

TABLE 3
Comparison of P release in anaerobic reactors (on mass basis) between R1 and R2, expressed as a percentage (R1/R2)

Period	M(Prel,R1)/M(Prel,R2), %				
	Mean	SD	n	95% upper confidence limit	95% lower confidence limit
3.2.2	116	27	5	150	82
3.2.3	98	12	9	106	89
3.2.4	86	14	15	94	78
3.2.5	76	2	6	78	74
3.2.6	90	3	9	92	88
3.2.7	100	18	5	122	77
3.2.8a	94	3	5	98	91
3.2.8b	83	4	4	90	76

SD: Standard deviation
n: no. of observations

P removal

Based on the observed P removals (P_{trem}) for the test and control systems, the difference in P removal was calculated and expressed as a molar ratio (mmol P_{trem}/ mmol Al_{dosed}). Statistical analysis of the results calculated on this basis for daily data pairs is given in Table 4.

Table 4 shows the average observed molar ratio of P_{trem}/ Al_{dosed} ranged from 0.22 to 0.71. However, variance in the P removal data was significant. At the low alum dose, it was not possible to determine the difference in P removal between the two systems with certainty due to the large standard deviations (Table 4). For example, for these periods (3.2.2 to 3.2.4), the lower 95% confidence limit of the molar ratio P_{trem}/ Al_{dosed} was close to zero (Table 4). At the higher alum dose, confidence in the data at the 95% level was greater, with the average molar ratio of P_{trem}/ Al_{dosed} ranging 0.53 to 0.71 and upper and lower 95% confidence limits ranging 0.57 to 0.85 (Table 4). On the basis of the results for Periods 3.2.5 and 3.2.6 in Table 4, alum dosing to the aerobic zone was not significantly more efficient than to the anaerobic zone, at the 95% confidence level using the F-test.

The data in Table 4 suggest that biological P removal was significantly inhibited in the test system during Period 3.2.8b,

TABLE 4
Summary of P removal due to alum dosing, as measured in the pilot plants. P_{trem} implies TP removal (Influent - Effluent). R1 : Alum dosed; R2: control

Period	Data	Al dose mmol/d	Zone	$\Delta P_{trem,R1}$ mgP/ℓ	$\Delta P_{trem,R2}$ 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 Al_{dosed}
3.2.2	Average	6.2	AE1	28.0	24.3	4.1	124	0.64
	n			18	17	17	17	17
	SD			7.2	8.7	7.6	298	1.55
	95% CL, upper			-	-	-	277	1.44
	95% CL, lower			-	-	-	-30	-0.15
3.2.3	Average	6.2	AE1	26.8	24.4	2.5	64	0.33
	n			27	27	27	27	27
	SD			8.6	7.7	5.0	178	0.93
	95% CL, upper			-	-	-	134	0.70
	95% CL, lower			-	-	-	-7	-0.03
3.2.4	Average	6.2	AN	26.4	25.3	1.3	42	0.22
	n			32	34	32	32	32
	SD			5.2	5.2	3.9	143	0.75
	95% CL, upper			-	-	-	94	0.49
	95% CL, lower			-	-	-	-10	-0.05
3.2.5	Average	12.4	AN	22.6	17.0	5.6	204	0.53
	n			9	9	9	9	9
	SD			3.9	3.5	0.9	33	0.09
	95% CL, upper			-	-	-	230	0.60
	95% CL, lower			-	-	-	179	0.46
3.2.6	Average	12.4	AE1	31.6	24.9	6.7	240	0.62
	n			10	10	10	10	10
	SD			6.5	6.9	0.9	38	0.10
	95% CL, upper			-	-	-	267	0.69
	95% CL, lower			-	-	-	212	0.55
3.2.7	Average	12.4	AE1	25.7	19.0	7.7	273	0.71
	n			21	19	18	18	18
	SD			5.9	6.7	3.0	110	0.29
	95% CL, upper			-	-	-	328	0.85
	95% CL, lower			-	-	-	218	0.57
3.2.8a	Average	12.4	AE1	26.0	18.8	7.5	270	0.70
	n			14	13	13	13	13
	SD			6.5	6.8	10.4	77	0.20
	95% CL, upper			-	-	-	317	0.82
	95% CL, lower			-	-	-	224	0.58
3.2.8b	Average	12.4	AE1	19.0	18.4	0.6	24	0.06
	n			8	8	8	8	8
	SD			3.4	4.9	4.1	155	0.40
	95% CL, upper			-	-	-	153	0.40
	95% CL, lower			-	-	-	-106	-0.27

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

resulting in virtually no net additional P removal due to alum. The influent alkalinity supplement had been withdrawn at the beginning of Period 3.2.8a (Table 1). Due to the shortness of this experimental period and the large variance in the P removal data, it cannot be concluded with certainty that the lower system alkalinity was the cause of the apparent inhibition in Period 3.2.8b. It is tempting to conclude that greater variance in the calculated difference in P removal between the test and control units during Period 3.2.8a arose from lower system alkalinity (i.e. that system alkalinity affected the stability of BEPR in the presence of alum dosing). *[Refer to **Appendix A** for pH and alkalinity data]*. However, variances for P removal in the two units separately was not significantly different from those for preceding periods with influent alkalinity supplement. Similarly, the difference in average P removal ($P_{trem,R1}$ - $P_{trem,R2}$) between Periods 3.2.8a and 3.2.8b (Table 4) was not statistically significant at the 95% confidence level using the F-test. The change in system alkalinity was therefore probably not the cause of the apparent deterioration in P removal in Period 3.2.8b. Other factors which were undetermined must have contributed to the response of the test unit in this period.

TABLE 5
Estimation of molar ratio of additional P removed as chemical precipitate versus alum dosed in pilot plants, based on fractionation (frac.) data

Unit/alum Period	Date	PCA, orthoP fraction (mgP/gVSS)	Ave. VSS for period (g/ℓ)	VSS wasted (g/d)	PCA orthoP fraction wasted (mgP/d)	Difference R1-R2 PCA orthoP wasted (mgP/d)	Al dosed (mmol/d)	mol P /mol Al from frac. data	mol P /mol Al (from Table 4)
R1: No Al: 3.2.1	28/8/94	18.15	2.734	4.374	79.40	11.77	0	-	-
R2: 3.2.1	28/8/94	17.79	2.376	3.802	67.63				
R1: Low Al, AE 1, 3.2.3	1/11/94	49.83	2.756	4.410	219.73	139.77	6.2	0.73	0.33 #
R2: 3.2.3	1/11/94	18.18	2.749	4.398	79.96				
R1: Low Al, AN, 3.2.4	19/12/94	54.97	2.422	3.875	213.02	138.88	6.2	0.72	0.22 #
R2: 3.2.4	19/12/94	19.42	2.386	3.818	74.14				
R1: High Al, AN, 3.2.5	8/1/95	80.04	2.11	3.376	270.22	219.58	12.4	0.58	0.53
R2: 3.2.5	8/1/95	16.56	1.911	3.058	50.63				
R1: High Al, AE 1, 3.2.6	22/1/95	89.61	2.105	3.368	301.81	232.77	12.4	0.61	0.62
R2: 3.2.6	22/1/95	22.65	1.905	3.048	69.04				
R1: High Al, AE 1, 3.2.8a	23/3/95	90.11	2.069	3.310	298.26	204.85	12.4	0.53	0.71
R2: 3.2.8a	23/3/95	30.97	1.885	3.016	93.41				
R1: High Al, AE 1, 3.2.8b	26/4/95	102.38	2.006	3.2096	328.60	271.53	12.4	0.71	0.06 #
R2: 3.2.8b	26/4/95	19.63	1.817	2.9072	57.07				

#: Difference in P removal between R1 and R2 for these periods not statistically significant at 95% confidence limit.

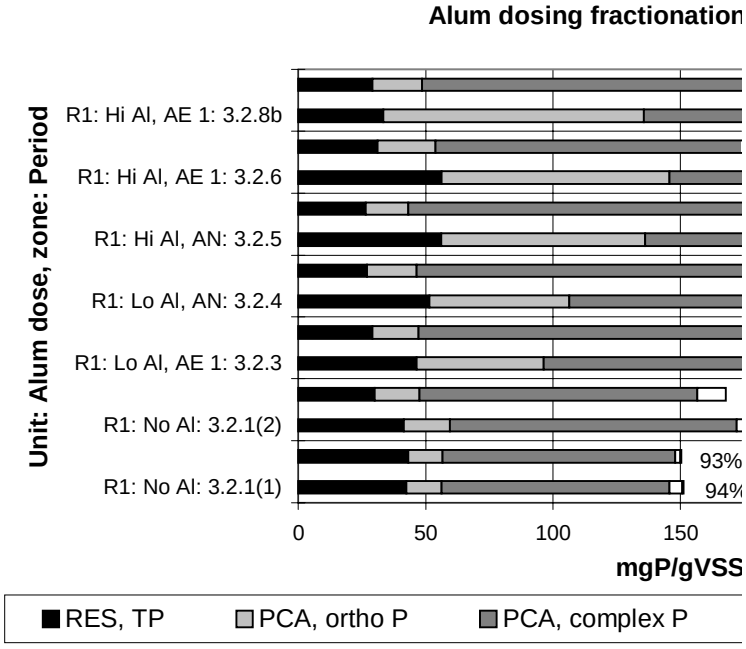


Figure 3
Fractionation results for alum dosing periods (3.2.1 to 3.2.8b).

Calculation of the average molar ratio of P_{trem}/Al_{dosed} in Table 4 is based on the assumption that the difference in P removal between R1 and R2 is only ascribable to chemical addition. The difficulty with this assumption is that the effects of both chemical and biological origin are lumped; if the biological mechanism was weaker in R1 than R2, it will reflect as a lower molar ratio of P_{trem}/Al_{dosed} but could be incorrectly interpreted as indicating less "efficient" precipitation. For this reason, an attempt was made to use data obtained by fractionation of the mixed liquor to estimate the additional P removal component in the test unit compared to the control. The fractionation data is discussed in more detail below. The orthoP content of the PCA extract (i.e. the fraction ascribed to

chemical precipitate) can be expressed on a molar basis relative to the alum dosed as an alternative method of estimating precipitation stoichiometry. In Table 5 these results are compared with those based on differences in system P removal (Table 4). Comparing the results in Table 5, it can be seen that the P/Al stoichiometry was relatively constant in the range 0.53 to 0.73 mol P/mol Al, whereas the results based on differences in P removal were more variable. Reasonably good agreement between the two methods was obtained for Periods 3.2.5, 3.2.6 and 3.2.8a during which the observed difference in P removal between the test and control units was statistically significant (Table 4).

Fractionation results

Fractionation results for the alum dosing periods (Periods 3.2.1 through 3.2.8 a&b) are summarised in Fig. 3. These results show that alum dosing had the effect of increasing the orthoP ("chemical precipitate") fraction by between 2.8 times (at the low alum dose) and 5.2-times (at the higher alum dose of 9 mg/ℓ as Al). The biggest increase in the orthoP fraction of the test versus control unit was for the high alum dose to the anaerobic zone (Period 3.2.5), implying that the chemical mechanism was relatively strong during this period. This agrees with the earlier observation of relatively reduced P release in the anaerobic reactor of the test unit compared to the control during this period (Table 3).

The PCA-extracted complex P (polyP) fraction decreased by 16% in the test unit when receiving a low alum dose (5 mg/ℓ as Al) to the aerobic zone, relative to the control (Table 6). This decrease was more pronounced (24%) with the low alum dose to the anaerobic zone, and very pronounced (37 to 40%) at the high alum dose (9 mg/ℓ as Al) to either the anaerobic or aerobic zones (Table 6). Concomitant with the decrease in the PCA complex P fraction, an increase in the residue total P was noted (Fig. 3). As a consequence, the fractionation procedure was later modified by inclusion of a NaOH extraction step after the PCA step (refer to **Part 2** - De Haas et al., 2000b). However, the NaOH step had not been included in the fractionation procedure used at this stage. Hence, the complex ("biological") P content of the residue fraction was estimated from the extent to which it registered P release in the anaerobic batch test. By addition, the total complex ("biological") P fractions of the PCA and residue fractions could be compared for the two units (Table 6). On this basis, the inhibition of the biological P fraction(s) in the test unit was 11 to 16% at the low alum dose, and 23 to 24% at the high alum dose. These results suggest a slightly higher degree of inhibition of the biological mechanism than that judged from P release in the anaerobic zone (compare with Table 3).

As noted in Table 2, new (semi-) enhanced cultures were re-developed during Period 3.2.7. The principal difference in operation of the units between Periods 3.2.7 and 3.2.8 (a/b) was the withdrawal of the influent bicarbonate supplement at the end of Period 3.2.7 (Tables 1 and 2). Table 6 shows that the biological (complex P) fractions were still increasing through Periods 3.2.8(a) and (b), suggesting that steady-state had not yet been achieved, despite the preceding period of three sludge ages at the same acetate feed concentration. This could explain the apparently higher biological P fractions in the test unit relative to the control in Period 3.2.8a (Table 6). However, approximately one month later (Period 3.2.8b), the biological fractions in the test unit were *less* than those of the control, suggesting inhibition due to alum (Table 6). The percentage inhibition (24%) was similar in Period 3.2.8(b) to that noted at the same alum dose for the previous cultures (Periods 3.2.5 and 3.2.6). Furthermore, Table 6 shows that the chemical P fraction had reached a large difference (more than five-fold) between the test and control units during Period 3.2.8(b). It is possible that the lower bicarbonate alkalinity of the system increased the efficiency of chemical precipitation mechanism with alumwhile having the opposite effect on the biological mechanism. In this regard, it is worth noting that the aerobic reactor pH (point of alum dosing) was between ~0.25 and 0.5 pH units lower during Periods 3.2.8a and b, compared to Periods 3.2.6 and 3.2.7 (Table A1, **Appendix A**). However, considering the brevity of Periods 3.2.6 and 3.2.8b, it is not possible to conclude with certainty whether a pH difference of this order had a significant impact on either mechanism.

Anaerobic batch P-release tests with excess acetate (Fig. 4), showed that most of the P release came from the PCA complex P fraction, However, in the test unit sludge, some P release also occurred from the residue fraction, such that the residue TP after P-release was similar to that of the control before the batch test. This provides justification for including the estimated complex P fraction of the residue with that of the PCA extract when estimating the total "biological" P component from fractionation results (Table 6). However, the apparent shift in solubility of the complex P fraction from the PCA extract to the residue (or alkaline extract, as later incorporated in the full fractionation procedure) is probably not significant in respect of the biological P removal mechanism *per se*. An experiment described in **Part 2** of this series of papers (De Haas et al., 2000b) clearly demonstrated that partitioning of complex P between the PCA and alkaline fractions is strongly influenced by the presence of metal ions during the fractionation test. In that experiment iron chloride artificially added during the fractionation test caused complex P to "move" from the PCA extract to the residue (or alkaline extract when applied). Aluminium ions would probably exert a similar effect. The resultant phosphorus fractionation pattern may be similar irrespective of whether the metal ions arise from the mixed liquor solids or from *in vitro* addition. Similarly, the apparent shift (or uptake) in complex P from the PCA fraction to the residue fraction for the control after the anaerobic batch P-release test, could be an artefact of the fractionation procedure and may not be biologically significant (Fig. 4).

Comparing orthoP release to the supernatant in anaerobic batch tests (Fig. 4), the test unit showed a depression of 7 to 17% for low alum dosing periods, compared to the control (Periods 3.2.3 and 3.2.4). For high alum dosing periods (Periods 3.2.5, 3.2.6 and 3.2.8b), the depression was 20 to 23 %. This is in good agreement with the results based on the estimated total biological fractions (Table 6), and similar or slightly higher than the mass balance results for P release in the anaerobic reactors of the test and control units themselves (Table 3).

Magnesium removal

Table 7 shows magnesium removal for all alum dosing periods during which it was measured.

From Table 7, the average molar ratio of Mg_{rem}/P_{trem} was higher in both the test and control units during Periods 3.1.6 and 3.2.8a than the other periods, although the larger standard deviations for these periods reduce confidence in the results. During these two periods, the system alkalinity was expected to be lower, either due to acid dosing or the absence of a bicarbonate supplement in the influent. Given the large variance in the magnesium removal data for these periods, the observed differences are not statistically significant (F-test, 99% confidence).

Excluding Periods 3.1.6 and 3.2.8a, Table 7 shows that the median molar ratio of Mg_{rem}/P_{trem} observed was 0.24 to 0.28. This is very close to the value of 0.26 reported by Wentzel et al. (1988) for batch P release and P uptake tests, implying that magnesium fraction serves as counter-ion to biologically stored polyP. Further-

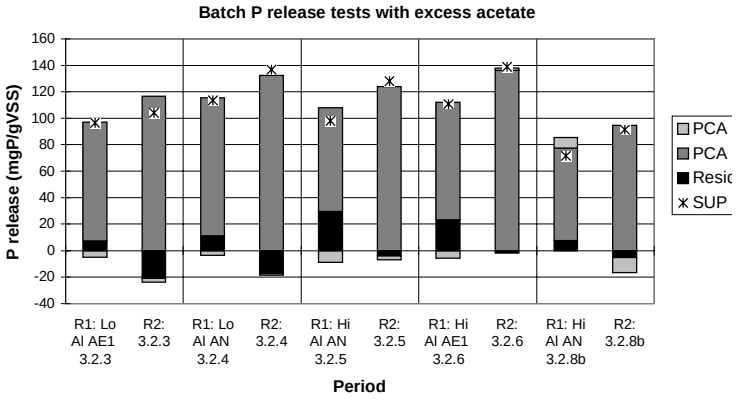
TABLE 6
Comparison of P fractionation data between test and control units during alum dosing periods (see also Fig. 3)

Date, Unit	Period	Alum dose Low = 5 mg/ℓ High = 9 mg/ℓ as Al based on influent	PCA Complex P mgP/gVSS	RES Complex P estimate * mgP/gVSS	Sum of PCA and RES Complex P fractions mgP/gVSS Note 1	PCA orthoP fraction mgP/gVSS Note 1	VSS during fraction-ation g/ℓ	Inhibition (-) or stimulation (+) of biological fractions (PCA + RES) % (R1/R2)	Inhibition (-) or stimulation (+) of biological PCA fraction only % (R1/R2)	Inhibition (-) or stimulation (+) of biological mechanism estimated from P release
		See Table 2 (zone dosed)	"Biological"	"Biological"	Total " Biological"	"Chemical"		Note 2	Note 2	See Table 3
16/8/94, R1 16/8/94, R2	**3.2.1**	**None** -	**89.47** 91.29	**0** 0	**89.47** (87%) 91.29 (87%)	13.88 **(13%)** 13.47 (13%)	**2.366** 2.452	-2% -	**-2%**	No data
28/8/94, R1 28/8/94, R2	**3.2.1**	**None** -	**112.70** 108.94	**4.69** 0	**117.39** (87%) 108.94 (86%)	18.15 **(13%)** 17.89 (14%)	**2.698** 2.459	+7% -	**+4%**	No data
1/11/94, R1 1/11/94, R2	**3.2.3**	**Low, AE1** -	**123.61** 147.48	**7.40** 0	**131.01** (72%) 147.48 (89%)	49.83 **(28%)** 18.18 (11%)	**2.569** 2.582	-11% -	**-16%**	-2%
19/12/94, R1 19/12/94, R2	**3.2.4**	**Low, AN** -	**122.55** 160.30	**11.36** 0	**133.91** (71%) 160.30 (89%)	54.97 **(29%)** 19.42 (11%)	**2.338** 2.256	-16% -	**-24%**	-14%
8/1/95, R1 8/1/95, R2	**3.2.5**	**High, AN** -	**106.14** 177.15	**29.60** 0	**135.74** (63%) 177.15 (91%)	80.04 **(37%)** 16.56 (9%)	**2.049** 1.836	-23% -	**-40%**	-24%
22/1/95, R1 22/1/95, R2	**3.2.6**	**High, AE1** -	**117.16** 185.16	**23.40** 0	**140.56** (61%) 185.16 (89%)	89.61**(39%)** 22.65 (11%)	**2.224** 2.034	-24% -	**-37%**	-10%
23/3/95, R1 23/3/95, R2	**3.2.8a**	**High, AE1** -	**55.04** 58.97	**14.68** 0	**69.72****(44%) 58.97**(66%)	90.11 **(56%)** 30.97 (33%)	**2.358** 2.131	+18% -	**-7%**	-6%
26/4/95, R1 26/4/95, R2	**3.2.8b**	**High. AE1**	**101.97** 144.24	**7.73** 0	**109.7** (52%) 144.24 (88%)	102.38 **(48%)** 19.63 (12%)	**1.994** 1.865	-24% -	**-29%**	-17%

* Estimate based on P release from RES fraction during batch tests, assuming P released (after - before batch test) = Complex P. Apparent uptake in some fractions after batch test, ignored since this was considered to be artefact of the fractionation method (see text).
** New enhanced culture developed in Period 3.2.7; biological mechanism not fully developed in Period 3.2.8a.
Note 1: (%) Percentages in parentheses refer to % sum of "Total Biological" and "Chemical".
Note 2: Percentages refer to percent inhibition (e.g.-2%) or stimulation (e.g. +4%) of R1 fractions (mgP/gVSS), relative to R2.

Figure 4

Fractionation results for periods with alum dosing using anaerobic batch P release test in the presence of excess acetate. P release for sludge fractions represents the difference between the "size" of the respective fractions before vs. after the anaerobic batch test. Negative release (apparent uptake) in PCA orthoP or residue fractions suggests precipitation (or complexation) of a portion of biologically released P, and may considered to be an artefact of fractionation method (refer to text).



more, on the basis of the magnesium data, inhibition of the biological P removal mechanism in the presence of alum dosing was approx. 0.04 mol Mg_{rem}/mol P_{trem} on average during Periods 3.2.2 through 3.2.7. This suggests that the biological mechanism was on average inhibited 16% during these periods (Table 7), which is in approximate agreement with the results from fractionation data (based on the combined biological fractions in Table 6). Neglecting Periods 3.1.6 and 3.2.8a due to the large standard deviations in the magnesium data, fair agreement was obtained between the ratio of Mg/P removal stoichiometry (R1/R2) in Table 7 and the equivalent ratio in terms of P release on a mass basis (Table 3). When the most inhibition of P release in R1 was noted (Period 3.2.5 from Table 3), the Mg/P removal ratio in R1 was lowest, relative to R2 (Table 7), and *vice versa*.

TABLE 7
Magnesium removal data for alum dosing periods. ND: Not determined

Period	Data	Al dose mmol/d	Zone	Observed Stoichiometry Mg removed/ P removed (mol/mol)		Ratio
				R1	R2	R1/R2 (%)
3.1.6	Average n SD	6.2	AE1	0.34 13 0.20	0.36 13 0.13	91% 13 35%
3.2.2	Average n SD	6.2	AE1	0.22 7 0.04	0.24 6 0.05	92% 6 19%
3.2.3	Average n SD	6.2	AE1	0.23 11 0.08	0.26 11 0.04	87% 11 38%
3.2.4	Average n SD	6.2	AN	0.28 10 0.05	0.35 11 0.09	82% 10 11%
3.2.5	Average n SD	12.4	AN	0.21 3 0.03	0.31 3 0.05	69% 3 4%
3.2.6	Average n SD	12.4	AE1	0.24 3 0.06	0.28 3 0.03	84% 3 13%
3.2.7	Average n SD	12.4	AE1	0.28 3 0.15	0.28 2 -	101% 2 -
3.2.8a	Average n SD	12.4	AE1	0.38 5 0.10	0.54 4 0.14	75% 4 12%
Overall median				0.26	0.30	88%
Median excluding Periods 3.1.6 and 3.2.8a				0.24	0.28	84%

Sludge production

The observed VSS and TSS data for alum dosing periods are given in Table 8. The VSS data suggest that the low alum dose resulted in an increase in VSS production of less than 13%, while the higher alum dose gave an increase in VSS of 10 to 17%. However, variance in the solids data reduces confidence in these estimates, particularly since the difference in VSS between the two units was small (<300 mg/ℓ) in comparison to the means and standard deviations (Table 8).

From the data in Table 8, the inorganic suspended solids (ISS) may be calculated:

ISS = TSS - VSS

Furthermore, the difference in ISS (ΔISS) between the two units (R1 and R2) can be calculated. It may be expected that ΔISS would arise from the chemical precipitate due to alum dosing. Hence, it is possible to compare the observed ΔISS with estimates of precipitate formation based on the additional P removal in R1 (ΔPt_{rem}, see Table 4). In order to do this, the stoichiometry of the precipitate must either be assumed or estimated. An estimate may be obtained from taking the molar ratio of alum dosed to ΔPt_{rem} (Table 4), on the assumption that all the metal is removed through precipitation reactions and becomes bound in the mixed liquor matrix. Ideally the precipitation of phosphate with aluminium would be stoichiometric as $AlPO_4$ (1 mol Aℓ/ mol P). If the observed stoichiometry is >1 mol Al_{dosed}/ mol P_{trem}, then it may be assumed that some mixture of aluminium

TABLE 8
Mixed liquor TSS and VSS results for alum dosing periods. Mean (± SD)

Period Unit	Days (Alum dose, mg/ℓ as Al)	TSS mg/ℓ	ΔTSS (R1-R2)/R2 %	VSS mg/ℓ	ΔVSS (R1-R2)/R2 %
3.2.2 R1	26 days 5 mg/ℓ AE1	5076 (153)	17%	3040 (101)	13%
3.2.2 R2	26 days 0 mg/ℓ	4222 (301)	-	2693 (154)	-
3.2.3 R1	40 days 5 mg/ℓ AE1	4946 (356)	6%	2756 (241)	0%
3.2.3 R2	40 days 0 mg/ℓ	4649 (248)	-	2749 (152)	-
3.2.4 R1	49 days 5 mg/ℓ AN	4654 (336)	7%	2422 (157)	2%
3.2.4 R2	49 days 0 mg/ℓ	4317 (260)	-	2386 (197)	-
3.2.5 R1	14 days 9 mg/ℓ AN	4198 (230)	14%	2110 (126)	10%
3.2.5 R2	14 days 0 mg/ℓ	3619 (167)	-	1911 (86)	-
3.2.6 R1	14 days 9 mg/ℓ AE1	4297 (324)	16%	2105 (259)	17%
3.2.6 R2	14 days 0 mg/ℓ	3603 (233)	-	1805 (117)	-
3.2.7 R1	31 days 9 mg/ℓ AE1	3922 (510)	21%	2095 (123)	11%
3.2.7 R2	31 days 0 mg/ℓ	3104 (231)	-	1894 (140)	-
3.2.8a R1	22 days 9 mg/ℓ AE1	4287 (156)	26%	2069 (102)	10%
3.2.8a R2	22 days 0 mg/ℓ	3187 (180)	-	1885 (123)	-
3.2.8b R1	10 days 9 mg/ℓ AE1	4215 (109)	31%	2006 (49)	10 %
3.2.8b R2	10 days 0 mg/ℓ	3217 (69)	-	1817 (37)	-

phosphate and aluminium hydroxide precipitation is probably taking place. A convenient chemical formula for the hypothetical aluminium hydroxy-phosphate precipitate may be written as:

$$Al_r\ PO_4\ OH_{(3r-3)}$$

where:

r = stoichiometry of Al:P (mol Aℓ/ mol P).

Furthermore, it should be noted that upon ashing (during VSS determination, at 550 °C), aluminium hydroxide will be converted to aluminium oxide (Power et al., 1992). On a similar basis to the typical conversion of $Al(OH)_3$ to Al_2O_3, the above-mentioned formula for aluminium hydroxy-phosphate converts to the following formula for hypothetical aluminium phosphate oxide:

$$Al_r\ PO_4\ O_{(1.5r-1.5)}$$

where:

r = stoichiometry of Al:P (mol Aℓ/ mol P)

Using the approach described above, the data in Table 9 were calculated.

From Table 9 it can be seen that the estimates of ΔISS from precipitation stoichiometry were of the same order of magnitude as the observed ΔISS. For five of the seven experimental periods examined, the recovery of estimated and observed ΔISS was in the range 77 to 119%. For Period 3.2.5 and 3.2.6, the observed ΔISS vales were smaller than the estimated values. This suggests that the experimental systems had not reached steady-state in terms of solids concentrations during these periods. The TSS and VSS (and hence ISS) in the systems can be expected to take several sludge ages to approach steady-state, responding more slowly than N & P and reflected only partially in the COD mass balances. Since the sludge age of the systems during alum dosing was 20 d, changes in the operational state of the unit(s) during these periods may have influenced the results in Table 9:

- Period 3.2.5: The alum dose to R1 was doubled at the start of this period and the period was short (14 d, or less than one sludge age). Although this period was sufficient to observe the immediate response in terms of additional (chemical) P removal, it was probably not sufficiently long to observe the new steady state ISS in R1.
- Period 3.2.6: This period followed immediately on from Period 3.2.5 with a change of alum dosing point and was also of short duration (14 d).

Summarising, the data in Table 9 suggest that increase in ISS due to alum dosing may be estimated with reasonable certainty (<8% error relative to TSS in test unit) using the above-mentioned hypothetical chemical formulae and the observed stoichiometry of aluminium dosed relative to additional P removal.

It is worth noting here that bicarbonate alkalinity consumption due to chemical dosing (based on the difference in effluent bicarbonate alkalinity between the test and the control units) was approximately 2.24 mmol Alk./mmol Al dosed, which is lower than the theoretical value of 3.0 mmol Alk./mmol Al for the precipitation of pure $Al(OH)_3$ (Loewenthal et al., 1986). This suggests that the aluminium precipitate formed involved fewer than 3 mol OH/ mol Al. When combined with the average P:Al stoichiometry in the range ~0.5 to ~0.75 mol P/mol Al (Table 5, from fractionation), these data suggest that an average approximate formula for the aluminium hydroxy-phosphate complex formed could lie in the following range:

$$Al_2(X^{2+})\ PO_4(OH)_5$$
$$Al_{1.66}(X^{2+})\ PO_4(OH)_4 \text{ (average)}$$
$$Al_{1.33}(X^{2+})\ PO_4(OH)_3$$

where X^{2+} is some unknown (possibly divalent) cation such as Mg^{2+} or Ca^{2+} (see Arvin, 1985). This compares with the generalised

TABLE 9
Comparison of observed ISS and that predicted from chemical P removal for alum dosing periods. For all experimental periods, sludge age (Rs) = 20 d. ISS = TSS - VSS (see data in Table 8).

	Observed ISS Table A2	Observed ISS Table A2	Observed Δ ISS	$\Delta M P_{trem}$ Table 4	Stoichio-metry Observed Table 4	*Stoichio-metry Observed*	Estimate from *Stoichio-metry observed*	Estimated ΔISS from *Stoichio-metry observed*	Estimate/ Observed
Period (duration) Alum dose	**mg/ℓ**	**mg/ℓ**	**mg/ℓ**	**mg P/d**	**mol P_{rem}: mol Al_{dosed}**	**mol Al_{dosed} : mol P_{rem}**	***Al~P~OH*** **Note 1**	**Al~P~O** ***Note 2***	***Al~P~O/*** **ΔISS**
Unit:	**R1**	**R2**	**R1-R2**	**R1-R2**	**P:Al**	***Al:P***	**mg/ℓ**	**mg/ℓ**	**%**
3.2.2 (26 d) 5 mg/ℓ Al, AE1	2036	1529	**507**	135.0	0.70	*1.43*	423	**392**	77%
3.2.3 (40 d) 5 mg/ℓ Al, AE1	2190	1900	**290**	65.6	0.34	*2.94*	362	**292**	101%
3.2.4 (49 d) 5 mg/ℓ Al, AN	2232	1931	**301**	33.9	0.18	*5.56*	326	**242**	80%
3.2.5 (14 d) 9 mg/ℓ Al, AN	2088	1708	**380**	216.8	0.57	*1.75*	790	**701**	185%
3.2.6 (14 d) 9 mg/ℓ Al, AE1	2192	1798	**394**	238.8	0.62	*1.61*	817	**738**	187%
3.2.7 (31 d) 9 mg/ℓ Al, AE1	1827	1210	**617**	237.1	0.62	*1.61*	812	**733**	119%
3.2.8a (22 d) 9 mg/ℓ Al, AE1	2218	1302	**916**	263.7	0.69	*1.45*	835	**770**	84%

AN = Anaerobic zone; AE1 = First aerobic zone
Note 1: Al~P~OH : hypothetical metal hydroxy-phosphate, $Al_r PO_4 OH_{(3r-3)}$
Note 2: Al~P~O : hypothetical metal phosphate oxide, $Al_r PO_4 O_{(1.5r - 1.5)}$

formula used by Luedecke et al. (1989) and Briggs (1996) which will predict less alkalinity loss per mol Al, namely:

$$Al_r PO_4 (OH)_{(3r-3)}$$

Conclusions

- Under conditions in which P was never limiting, simultaneous alum dosing always resulted in additional (chemical) P removal in the presence of a strong biological P removal mechanism using semi-enhanced cultures over experimental periods of 0.7 to 2.5 sludge ages each (total up to 7 sludge ages). However, evidence of partial inhibition of the biological mechanism emerged. This evidence may be summarised as follows:
  - Mass balance considerations showed that, compared to the control (R2), the average mass of P release in the anaerobic reactor of the test unit (R1) was initially little affected by a low dose of alum, but in subsequent experimental periods at higher alum dose apparent inhibition of P release was noted. At the higher alum dose (9 mg/ℓ as Al, based on influent), the degree of inhibition was approximately 10% when dosed to the aerobic zone and up to 25% when dosed to the anaerobic zone. It is possible that alum dosing to the anaerobic zone resulted in precipitation of a portion of the biologically released P. However, measurements of magnesium relative to P removal tended to support the P release data. Inhibition of the biological mechanism by ~8 to 30% was indicated from the magnesium results, although variance in the data precluded confident interpretation of the results.
  - Relative to the control, fractionation studies showed that the PCA-extracted complex P (polyP) fraction of the mixed liquor solids decreased in the test unit when dosed with alum. At the low alum dose (5 mg/ℓ as Al), this decrease was 16% when the aerobic zone was dosed, and more pronounced (24%) when the anaerobic zone was dosed. At high alum dose (9 mg/ℓ as Al) the decrease was very pronounced (37 to 40%). However, the decrease in the PCA complex P fraction was accompanied by an increase in the residue P fraction. Batch P release tests showed the increased residue fraction was biologically active. The combined result of estimated Complex P (PCA extract + residue) was therefore taken as representing the "total biological P" (including polyP) stored by the cells. On this basis, the fractionation results showed that the degree of inhibition of the biological mechanism was: 11% for the low alum dose to the aerobic zone; 16% for a low alum dose to the anaerobic zone; and 23 to 24% for a high alum dose to either the aerobic or anaerobic zone.
  - The magnitude of P release in anaerobic batch tests (with excess acetate present) for mixed liquor from for the test unit (alum dosed) was compared to that from the control.

It was found that P release for the samples from the test unit was depressed by 7 to 17% for the periods with low alum dose and by 20 to 23% for the periods with high alum dose.

- The observation of a degree of inhibition of the BEPR mechanism under conditions where a large excess of orthoP was present in the effluent suggests that the biological mechanism functions less well in the presence of the simultaneous precipitation mechanism. The orthoP concentration in the bulk liquid phase of the mixed liquor may not be representative of the localised orthoP concentration in close proximity to the sludge floc when associated with chemical precipitate.
- Fractionation results showed that there was a tendency for alum to increase the sludge orthoP fraction, which may be explained as increased formation of chemical precipitate. The increase in this fraction was greatest for periods which showed the greatest inhibition (or depression) of the biological (complex P) fractions. This suggests that the chemical precipitation mechanism is somewhat antagonistic towards the biological mechanism, even when the reactor (or effluent) phosphate concentration is not limiting.
- Strictly speaking, where the biological mechanism in the test unit may be partially inhibited by the chemical mechanism, the P:Al stoichiometry of simultaneous chemical precipitation cannot be estimated by taking the difference between the system P removal of a test system (chemically dosed) versus a control (not chemically dosed). Nevertheless, this method provides an estimate of the overall "precipitation efficiency". Phosphorus fractionation provided an alternative means of estimating the stoichiometry of precipitation from chemical dosing, on the assumption that the orthoP content of the cold PCA fraction originates (principally) from chemical precipitate. It also makes allowance for background levels of precipitates present in the control system as a result of natural processes for a given sewage. On this basis, the average estimated stoichiometry of the precipitate from alum was found to be between approximately 0.5 and 0.73 mol P/ mol Al. This is somewhat less than the stoichiometric amount of 1 mol P/ mol Al for the "ideal" precipitate $AlPO_4$.
- Observations of actual alkalinity losses attributable to alum dosing suggested that the average formula for chemical precipitate from alum could involve another (unknown) cation in a theoretical average formula of: $Al_{1.33}(X^{2+})\ PO_4\ (OH)_3$. However, in the absence of further substantive evidence for this proposal, the use of the generalised precipitate formula $Al_rPO_4OH_{(3r-3)}$ appeared to be acceptable for the purposes of ISS (or TSS) estimation.
- Sludge production showed a small increase in VSS in the test unit relative to the control (<1 to 17% on average) in the presence of alum dosing. TSS production showed larger increases (6 to 31% on average) with alum dosing. The increased TSS was expected from the additional mass of chemical precipitate (i.e. ISS) present in the mixed liquor as a result of alum addition. As a practical approximation, the increase in ISS due to chemical precipitate could be predicted on the basis of the additional system P removal and the observed stoichiometry relative to a known alum dose.

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References

ARVIN E (1985) Biological removal of phosphorus from wastewater. *CRC Critical Reviews in Environmental Control* **15** 25 - 64.

BRIGGS TA (1996) Dynamic Modelling of Chemical Phosphorus Removal in the Activated Sludge Process. M. Eng. Thesis, School of Graduate Studies, McMaster Univ., Hamilton, Ontario, Canada.

BROWN MJ and LESTER JN (1979) Metal removal in activated sludge: The role of bacterial extracellular polymers. *Water Res.* **13** 817-837.

BURKE RA, DOLD PL and MARAIS GvR (1986*)* Biological Excess Phosphorus Removal in Short Sludge Age Activated Sludge Systems. Report No. W58. Univ. of Cape Town, Depts. of Chem. Eng. and Civil Eng., December 1986.

CLAYTON JA, EKAMA GA, WENTZEL MC and MARAIS GvR (1989) Denitrification Kinetics in Biological Nitrogen and Phosphorus Removal Activated Sludge Systems. Research Report W63, Dept. of Civil Eng., Univ. of Cape Town, Rondebosch, Cape Town.

DE HAAS DW, WENTZEL MC and EKAMA GA (2000a) The use of simultaneous mical precipitation in modified activated sludge systems exhibiting biological enhanced phosphate removal. Part 1: Literature review. *Water SA* **26** (4) 439-452.

DE HAAS DW, WENTZEL MC and EKAMA GA (2000b) The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological enhanced phosphate removal. Part 2: Method development for fractionation of phosphate compounds in activated sludge. *Water SA* **26** (4) 453-466.

EKAMA GA and MARAIS GvR (1984) Two improved activated sludge settleability parameters. *IMIESA* (June) 20-25.

GERBER A, DE VILLIERS RH, MOSTERT ES and VAN RIET CJJ (1987) The phenomenon of simultaneous phosphate uptake and release, and its importance in biological nutrient removal. In: Ramadori R (ed.) *Advances in Water Pollution Control: Biological Phosphate Removal from Wastewaters.* Pergamon, Oxford. 123-134.

LOEWENTHAL RE, WIECHERS HNS and MARAIS GvR (1986) Softening and Stabilization of Municipal Waters. Water Research Commission, Pretoria.

LUEDECKE C, HERMANOWICZ SH and JENKINS D (1989) Precipitation of ferric phosphate in activated sludge: A chemical model and its verification. *Water Sci. Technol*. **21** (Brighton) 325-327.

MEIRING & BARNARD (1990) First Interim Report on Upgrading of Darvill Wastewater Treatment Plant. Report to City Eng. Dept., Pietermaritzburg by Wates Meiring Barnard (formerly Meiring & Barnard), Midrand, Johannesburg, South Africa.

POWER SPB, EKAMA GA, WENTZEL MC and MARAIS GvR (1992) Chemical Phosphorus Removal from Municipal Wastewater by the Addition of Waste Alum Sludge to the Activated Sludge System. Research Report No. W66, Univ. of Cape Town, Dept. of Civil Eng.

RANDALL EW, WILKINSON A and EKAMA GA (1991) An instrument for the direct determination of oxygen utilisation rate. *Water SA* **17** (1) 11-18.

SLATTER NP and ALBOROUG, H (1990) Chemical oxygen demand using microwave digestion: A tentative new method. *Water SA* **18** (3) 145-148.

SMOLDERS GJF, VAN DER MEIJM J, VAN LOOSDRECHT MCM and HEIJNEN JJ (1994) Model of the anaerobic metabolism of the biological phosphorus removal process: Stoichiometry and pH influence. *Biotechnol. and Bioeng.* **43** 461-470.

STANDARD METHODS (1985) *Standard Methods for the Examination of Water and Wastewater* (16th edn.) American Public Health Association, Washington DC.

WENTZEL MC, LOEWENTHAL RE, EKAMA, GA and MARAIS, GvR. (1988) Enhanced polyphosphate organism cultures in activated sludge systems - Part 1: Enhanced culture development. *Water SA*, 14 (2), 81-92.

WENTZEL MC, LÖTTER LH, LOEWENTHAL RE and MARAIS GvR (1986) Metabolic behaviour of *Acinetobacter* spp. in enhanced biological phosphorus removal - A biochemical model. *Water SA* **12** 209-224.

WIECHERS HNS (ed.) (1987) *Guidelines for Chemical Phosphate Removal from Municipal Waste Waters.* Collaborative publication compiled by staff of the Town Council of Boksburg, City Council of Pretoria, National Institute of Water Research and the Water Research Commission. Water Research Commission, Pretoria.

WLPU-WMB (1993) *Darvill Wastewater Treatment Works: Future Extensions.* Joint Report by Knight Piesold (formerly Watermeyer Legge Piesold Uhlmann, WLPU) and Wates Meiring Barnard (WMB) to Umgeni Water, November 1993. Knight Piesold, Pietermaritzburg, South Africa.

TABLE A1
Summary pH (and bicarbonate alkalinity) data for Periods 3.2.1 to 3.2.8b.
Data in *italics* indicates mean instead of median.

Period (days) R1 Al dose	Unit:	R1	R2	R1	R2	R1	R2	R1 Effluent	R2 Effluent
	Zone:	AN	AN	AE1	AE1	AE2	AE2	H_2CO_3* Alk. (mg/ℓ as $CaCO_3$)	H_2CO_3* Alk. (mg/ℓ as $CaCO_3$)
3.2.1	Median	-	-	7.35	7.32	7.6	7.55	-	-
(13 d)	Min.	-	-	7.05	7.02	7.15	7.08	-	-
R1: 0 mg/ℓ	Max.	-	-	7.57	7.47	7.87	7.87	-	-
3.2.2	Median	-	-	7.27	7.28	7.48	7.50	-	-
(26 d)	Min.	-	-	7.15	7.15	7.28	7.25	-	-
R1: 5 mg/ℓ	25% ile	-	-	7.23	7.24	7.44	7.42	-	-
AE1 zone	75% ile	-	-	7.32	7.30	7.52	7.53	-	-
	Max.	-	-	7.48	7.48	7.71	7.84	-	-
3.2.3	Median	-	-	7.38	7.33	7.58	7.62	-	-
(40 d)	Min.	-	-	7.01	6.90	7.03	6.97	-	-
R1: 5 mg/ℓ	25% ile	-	-	7.34	7.30	7.55	7.57	-	-
AE1 zone	75% ile	-	-	7.42	7.39	7.64	7.65	-	-
	Max.	-	-	7.59	7.57	7.83	7.90	-	-
3.2.4	Median	-	-	7.32	7.35	7.53	7.62	-	-
(49 d)	Min.	-	-	6.96	6.93	7.03	6.86	-	-
R1: 5 mg/ℓ	25% ile	-	-	7.30	7.32	7.50	7.58	-	-
AN zone	75% ile	-	-	7.38	7.39	7.61	7.67	-	-
	Max.	-	-	7.52	7.51	7.78	7.81	-	-
3.2.5	Median	6.98	7.01	7.33	7.41	7.49	7.62	-	-
(14 d)	Min.	6.83	6.96	7.19	7.34	7.31	7.49	-	-
R1: 9 mg/ℓ	25% ile	6.94	6.97	7.31	7.37	7.40	7.56	-	-
AN zone	75% ile	7.09	7.08	7.39	7.45	7.50	7.66	-	-
	Max.	7.18	7.17	7.42	7.52	7.58	7.70	-	-
3.2.6	Median	7.11	7.02	7.58	7.60	7.65	7.70	-	-
(14 d)	Min.	7.04	6.94	7.47	7.53	7.52	7.61	-	-
R1: 9 mg/ℓ	25% ile	7.08	6.97	7.54	7.59	7.59	7.68	-	-
AE1 zone	75% ile	7.16	7.05	7.63	7.63	7.68	7.72	-	-
	Max.	7.24	7.13	7.67	7.70	7.76	7.86	-	-
3.2.7	Median	7.28	7.30	7.51	7.50	7.62	7.65	*281*	*319*
(31 d)	Min.	7.09	7.04	7.09	7.15	7.18	7.24	265	303
R1: 9 mg/ℓ	25% ile	7.21	7.22	7.41	7.40	7.56	7.57	-	-
AE1 zone	75% ile	7.35	7.36	7.56	7.59	7.68	7.75	-	-
	Max. #	9.49	9.88	8.51	8.71	8.40	8.45	301	326
3.2.8a	Median	7.00	6.95	7.25	7.20	7.32	7.37	*144*	*178*
(22 d)	Min.	6.75	6.80	6.87	6.99	6.81	7.01	110	145
R1: 9 mg/ℓ	25% ile	6.98	6.92	7.10	7.13	7.20	7.27	-	-
AE1 zone	75% ile	7.08	6.99	7.30	7.26	7.42	7.49	-	-
	Max.	7.26	7.24	7.53	7.60	7.67	7.80	229	265
3.2.8b	Median	7.01	6.95	7.07	7.11	7.17	7.28	*114*	*157*
(10 d)	Min.	6.77	6.76	6.90	7.04	6.98	7.23	92	132
R1: 9 mg/ℓ	25% ile	6.98	6.89	7.04	7.07	7.09	7.25	-	-
AE1 zone	75% ile	7.03	7.00	7.14	7.22	7.19	7.43	-	-
	Max.	7.05	7.19	7.16	7.58	7.29	7.88	136	182

:Sewage on 7/3/95 contained a slug of lime due to an operational fault on the full-scale plant.

TABLE A2
Pilot plant results for second experimental period during which alum was dosed to R1. R2 = control.
Results are averages with sample standard deviations in parentheses.

Period Unit	Days (Al dose,	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	DSVI mℓ/g	fPt,a mgP/ℓ	fPt,d mgP/ℓ	fPt,b1 mgP/ℓ	fPt,b2 mgP/ℓ
3.2.2 R1	26 days 5 mg/ℓ AE1	478 (61)	25 (2)	40.3 (6.3)	2.67 (0.64)	0.30 (0.23)	2.8 (0.78)	53.06 (2.01)	25.07 (7.73)	27.99 (7.20)	177.5 (10.2)	5076 (153)	3040 (101)	82 (7)	123.0 (9.7)	65.9 (4.9)	44.9 (4.5)	31.5 (3.6)
3.2.2 R2	26 days 0 mg/ℓ	478 (61)	26 (3)	40.3 (6.3)	2.92 (0.56)	0.27 (0.19)	2.43 (0.93)	53.06 (2.01)	28.91 (8.68)	24.25 (8.68)	155.9 (11.7)	4222 (301)	2693 (154)	84 (7)	111.6 (10.8)	66.1 (7.5)	46.4 (5.8)	34.5 (6.5)
3.2.3 R1	40 days 5 mg/ℓ AE1	379 (56)	23 (3)	38.3 (12.3)	3.80 (1.81)	0.57 (0.2)	7.63 (2.16)	49.67 (2.37)	22.83 (8.76)	26.84 (8.56)	215.8 (24.4)	4946 (356)	2756 (241)	79 (8)	114.2 (12.8)	57.4 (9.1)	35.3 (9.2)	23.3 (9.2)
3.2.3 R2	40 days 0 mg/ℓ	379 (56)	22 (4)	38.3 (12.3)	3.68 (2.02)	0.42 (0.17)	5.78 (1.84)	49.67 (2.37)	25.29 (8.10)	24.38 (7.66)	185.1 (21.8)	4649 (248)	2749 (152)	79 (5)	114.9 (12.0)	59.2 (8.90)	37.2 (9.4)	24.6 (9.0)
3.2.4 R1	49 days 5 mg/ℓ AN	346 (57)	22 (4)	38.3 (9.3)	2.32 (1.45)	1.07 (1.28)	4.71 (2.16)	49.00 (2.75)	22.67 (4.97)	26.37 (5.23)	242.0 (16.9)	4654 (336)	2422 (157)	66 (14)	96.2 (11.6)	51.8 (7.4)	32.0 (5.3)	22.1 (5.4)
3.2.4 R2	49 days 0 mg/ℓ	346 (57)	20 (2)	38.3 (9.3)	2.44 (2.09)	0.79 (1.03)	3.28 (1.24)	49.00 (2.75)	23.72 (4.42)	25.28 (5.19)	223.5 (19.9)	4317 (260)	2386 (197)	81 (16)	107.3 (11.4)	58.0 (8.2)	36.0 (5.3)	24.1 (4.2)
3.2.5 R1	14 days 9 mg/ℓ AN	251 (33)	18 (2)	31.9 (8.8)	2.09 (0.48)	0.46 (0.19)	5.84 (1.34)	46.71 (2.88)	24.14 (5.21)	22.57 (3.87)	267.4 (7.5)	4198 (230)	2110 (126)	71 (4)	70.6 (11.6)	41.3 (5.6)	28.8 (3.4)	22.8 (3.7)
3.2.5 R2	14 days 0 mg/ℓ	251 (33)	16 (3)	31.9 (8.8)	1.93 (0.77)	0.43 (0.15)	6.03 (1.48)	46.71 (2.88)	29.74 (4.64)	16.69 (3.49)	234.5 (36.4)	3619 (167)	1911 (86)	99 (4)	85.1 (13.0)	49.8 (6.3)	35.7 (3.5)	28.3 (3.1)
3.2.6 R1	14 days 9 mg/ℓ AE1	312 (56)	20 (2)	24.0 Estimate	2.5 Estimate	0.68 (0.65)	4.25 (0.78)	46.77 (1.98)	15.23 (4.99)	31.55 (6.48)	272.7 (14.7)	4297 (324)	2105 (259)	69 (3)	86.1 (4.8)	42.7 (3.7)	22.7 (5.2)	14.1 (5.3)
3.2.6 R2	14 days 0 mg/ℓ	312 (56)	18 (3)	24.0 Estimate	2.5 Estimate	0.49 (0.56)	5.08 (1.28)	46.77 (1.98)	21.89 (5.43)	24.88 (6.85)	245.1 (7.1)	3603 (233)	1805 (117)	101 (5)	95.4 (3.9)	45.3 (6.3)	30.1 (4.4)	21.8 (5.6)
3.2.7 R1	31 days 9 mg/ℓ AE1	350 (56)	16 (2)	31.0 (2.2)	2.16 (0.46)	0.00 (0.00)	4.80 (1.60)	47.02 (3.00)	21.41 (4.88)	25.66 (5.89)	162.4 (36.5)	3922 (510)	2095 (123)	52 (6)	71.6 (11.3)	40.5 (4.9)	28.5 (4.7)	22.4 (4.5)
3.2.7 R2	31 days 0 mg/ℓ	350 (56)	18 (3)	31.0 (2.2)	2.03 (0.55)	0.00 (0.01)	4.33 (1.6)	47.02 (3.00)	28.27 (6.20)	18.99 (6.73)	115.7 (13.7)	3104 (231)	1894 (140)	56 (7)	75.7 (11.1)	47.6 (8.7)	36.5 (6.0)	30.0 (5.3)
3.2.8a R1	22 days 9 mg/ℓ AE1	317 (15)	15 (4)	28.0 Estimate	2.25 (0.55)	0.37 (0.26)	4.35 (1.31)	45.31 (2.87)	19.63 (5.44)	26.00 (6.45)	245.3 (22.0)	4287 (156)	2069 (102)	52 (2)	73.9 (14.1)	39.5 (4.2)	26.3 (5.2)	18.3 (6.6)
3.2.8a R2	22 days 0 mg/ℓ	317 (15)	16 (5)	28.0 Estimate	2.30 (0.72)	0.25 (0.18)	3.62 (1.21)	45.31 (2.87)	26.75 (6.15)	18.84 (6.81)	169.3 (20.6)	3187 (180)	1885 (123)	55 (3)	80.4 (15.8)	48.8 (5.8)	33.6 (1.8)	24.8 (4.4)
3.2.8b R1	10 days 9 mg/ℓ AE1	301 (35)	20 (1)	25.3 (4.3)	3.67 (0.42)	0.90 (0.10)	6.54 (2.04)	45.79 (2.00)	26.80 (3.97)	18.99 (3.43)	274.8 (27.7)	4215 (109)	2006 (49)	54 (3)	80.9 (10.5)	47.8 (6.8)	35.0 (3.8)	29.1 (4.2)
3.2.8b R2	10 days 0 mg/ℓ	301 (35)	16 (1)	25.3 (4.3)	3.66 (1.16)	1.56 (0.27)	4.99 (1.58)	45.79 (2.00)	27.41 (6.18)	18.38 (4.92)	204.2 (14.2)	3217 (69)	1817 (37)	59 (4)	89.9 (12.3)	53.7 (6.1)	39.4 (3.9)	31.0 (3.5)

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

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TABLE A3
Mass balances for experimental Periods 3.2.2 to 3.2.8b. Sludge age (R_s) = 20 d

Period Unit	Days (Al dose, mg/ℓ Al)	Flow Qi, 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.	Ptrem mgP/ℓ	P/VSS mgP/gVSS	% P Bal.
3.2.2 R1	26 days 5 mg/ℓ AE1	34.8 (0.8)	3040 (101)	0.01 (0.01)	0.98 (0.6)	5.47 (1.56)	2.67 (0.64)	2.8 (0.78)	40.3 (6.3)	**90%**	18.84 (3.18)	478 (61)	25 (2)	**111%**	27.99 (7.2)	177.52 (10.15)	**89%**
3.2.2 R2	26 days 0 mg/ℓ	34.6 (4.2)	2693 (154)	0.01 (0.01)	1.25 (0.94)	7.51 (3.26)	2.92 (0.56)	2.43 (0.93)	40.3 (6.3)	**103%**	20.86 (4.42)	478 (61)	26 (3)	**112%**	24.25 (8.68)	155.85 (11.69)	**80%**
3.2.3 R1	40 days 5 mg/ℓ AE1	35.6 (0.7)	2756 (241)	0.07 (0.03)	2.86 (1.09)	7.64 (1.94)	3.8 (1.81)	7.63 (2.16)	38.3 (12.3)	**105%**	16.09 (1.81)	379 (56)	23 (3)	**109%**	26.84 (8.56)	215.8 (24.43)	**100%**
3.2.3 R2	40 days 0 mg/ℓ	36.5 (0.8)	2749 (152)	0.06 (0.03)	1.09 (0.85)	6.03 (1.89)	3.68 (2.02)	5.78 (1.84)	38.3 (12.3)	**105%**	16.60 (2.17)	379 (56)	22 (4)	**109%**	24.39 (7.66)	185.11 (21.77)	**91%**
3.2.4 R1	49 days 5 mg/ℓ AN	35.7 (2.3)	2422 (157)	0.03 (0.04)	0.99 (0.88)	3.34 (2.78)	2.32 (1.45)	4.71 (2.16)	38.3 (9.3)	**100%**	15.75 (2.24)	346 (57)	22 (4)	**111%**	26.37 (5.23)	242.01 (16.9)	**100%**
3.2.4 R2	49 days 0 mg/ℓ	35.9 (2.4)	2386 (197)	0.02 (0.04)	0.71 (0.47)	2.69 (1.35)	2.44 (2.09)	3.28 (1.24)	38.3 (9.3)	**94%**	15.42 (2.05)	346 (57)	20 (2)	**111%**	25.28 (5.19)	223.53 (19.91)	**94%**
3.2.5 R1	14 days 9 mg/ℓ AN	36.3 (0.3)	2110 (126)	0.05 (0.01)	2.48 (0.73)	5.97 (0.89)	2.09 (0.48)	5.84 (1.34)	31.9 (8.8)	**110%**	10.79 (0.59)	251 (33)	18 (2)	**113%**	22.57 (3.87)	267.38 (7.53)	**110%**
3.2.5 R2	14 days 0 mg/ℓ	36.1 (0.2)	1911 (86)	0.05 (0.02)	2.91 (0.49)	6.13 (0.86)	1.93 (0.77)	6.03 (1.48)	31.9 (8.8)	**130%**	12.10 (3.03)	251 (33)	16 (3)	**122%**	16.69 (3.49)	245.62 (9.98)	**130%**
3.2.6 R1	14 days 9 mg/ℓ AE1	35.8 (0.6)	2105 (259)	0.06 (0.07)	1.28 (0.46)	3.93 (0.80)	2.5 Estimate	4.25 (0.78)	24.0 Estimate	106% Estimate	13.20 (1.35)	312 (56)	20 (2)	**109%**	31.55 (6.48)	272.69 (14.74)	**81%**
3.2.6 R2	14 days 0 mg/ℓ	35.8 (0.7)	1805 (117)	0.04 (0.01)	2.20 (0.63)	4.38 (1.12)	2.5 Estimate	5.08 (1.28)	24.0 Estimate	95% Estimate	14.17 (1.48)	312 (56)	18 (3)	**108%**	24.88 (6.85)	245.07 (7.06)	**79%**
3.2.7 R1	31 days 9 mg/ℓ AE1	36.4 (0.6)	2095 (123)	0.03 (0.03)	1.96 (0.98)	5.11 (2.65)	2.16 (0.46)	4.80 (1.6)	31.0 (2.2)	**86%**	10.76 (1.35)	350 (56)	16 (2)	**87%**	25.66 (5.89)	162.35 (36.46)	**58%**
3.2.7 R2	31 days 0 mg/ℓ	36.7 (0.7)	1894 (140)	0.04 (0.84)	1.61 (1.91)	4.84 (2.83)	2.03 (0.55)	4.33 (1.6)	31.0 (2.2)	**84%**	11.37 (1.48)	350 (56)	18 (3)	**87%**	18.99 (6.73)	115.73 (13.65)	**50%**
3.2.8a R1	22 days 9 mg/ℓ AE1	36.3 (0.7)	2069 (102)	0.01 (0.01)	1.55 (0.91)	3.77 (1.25)	2.25 (0.55)	4.35 (1.31)	27.0 Estimate	**141%**	10.71 (1.55)	317 (77)	15 (4)	**84%**	26.00 (6.45)	245.30 (22.04)	**86%**
3.2.8a R2	22 days 0 mg/ℓ	36.1 (1.1)	1885 (123)	0.0 (0.0)	0.65 (0.53)	3.08 (0.8)	2.30 (0.72)	3.62 (1.21)	27.0 Estimate	**97%**	11.05 (1.96)	317 (77)	16 (5)	**90%**	18.84 (6.81)	169.32 (20.58)	**75%**
3.2.8b R1	10 days 9 mg/ℓ AE1	36.9 (0.4)	2006 (49)	0.0 (0.0)	3.55 (1.09)	6.48 (1.81)	3.67 (0.42)	6.54 (2.04)	273 (4.3)	**156%**	10.39 (1.17)	301 (35)	20 (1)	**84%**	18.99 (3.43)	274.75 (27.67)	**89%**
3.2.8b R2	10 days 0 mg/ℓ	36.6 (1.5)	1817 (37)	0.0 (0.0)	2.32 (1.25)	5.04 (1.93)	3.66 (1.16)	4.99 (1.58)	25.3 (4.3)	**99%**	11.12 (1.13)	301 (35)	16 (1)	**92%**	18.38 (4.92)	204.18 (14.19)	**88%**
									Mean: S.D.:	**106% 20%**			Mean: S.D.:	**102% 13%**		Mean: S.D.:	**88% 19%**