

other run. Dissolved CO₂ and/or methane, which are produced in anaerobic digestion, may have accumulated in the liquid, which was quiescent, during this time. Agitation, pumping, and contact with the bed may have then stimulated the gases to effervesce in the crystallizer feed line and reactor itself.

The possible weak upward trend noted in dissolved OP reduction through the series cannot be correlated well with any other observed trends with the possible exception of bed fineness. Bed fineness, as earlier discussed, could increase phosphorus removal by providing greater surface area to complete the reaction. However, the increasing removal of OP should be reflected also in TP, which instead shows two peaks, with the last several runs on a downward trend.

Results in the MVRs and Discussion

Overview of MVR Results

The results in the second stage, which consisted of one series of three multi-variate runs (MVRs), demonstrated some differences in phosphorus reduction among the condition sets tested. The condition sets were arranged factorially and randomized into three complete blocks, each block corresponding with a run; therefore, statistical analyses were straightforward. The analyses showed with high confidence that phosphorus reduction correlates positively with ammonia addition and with Mg addition up to a point. It showed little correlation with liquid flow rate.

Detailed Results

Figures 28 through 30 illustrate reduction achieved in OP at 41.2 L/h liquid flow rate. Each of the three figures corresponds with one ammonia addition level, and includes all nine results (three blocks with three Mg addition levels). Figures 31 through 33 depict the analogous results for TP reduction. Figures 34 through 39 present, in the same order and format, the data taken at 56.8 L/h.

Two trends can be observed in the figures. First, there is a general upslope in the plots, indicating higher reduction in both OP and TP at higher Mg addition rates. The trend often looks stronger in going from 0 to 30 ppm Mg than in going from 30 ppm to 60 ppm. Second, higher

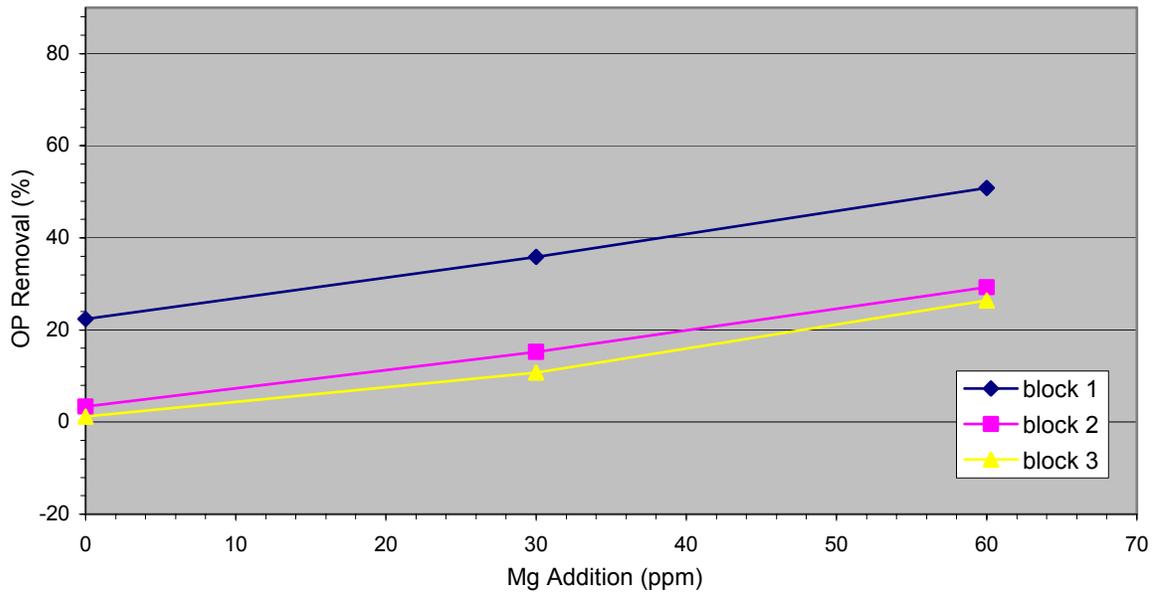


Figure 28: MVRs: OP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 41.2 L/h Flow

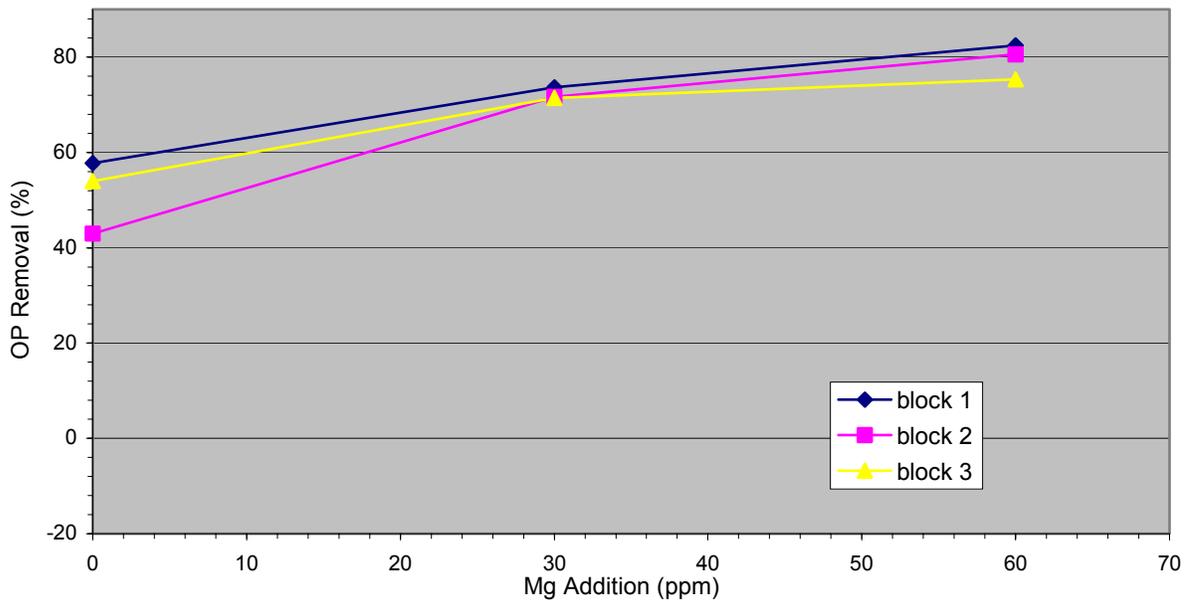


Figure 29: MVRs: OP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as TAN) Ammonia Addition and 41.2 L/h Flow

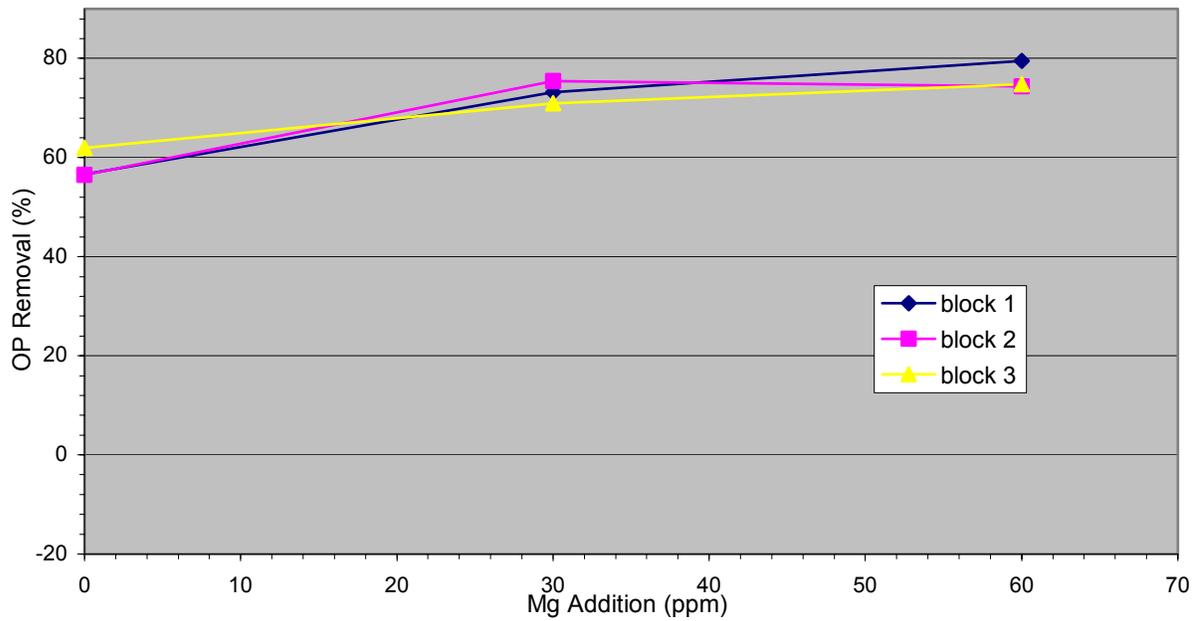


Figure 30: MVRs: OP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as TAN) Ammonia and 41.2 L/h Flow

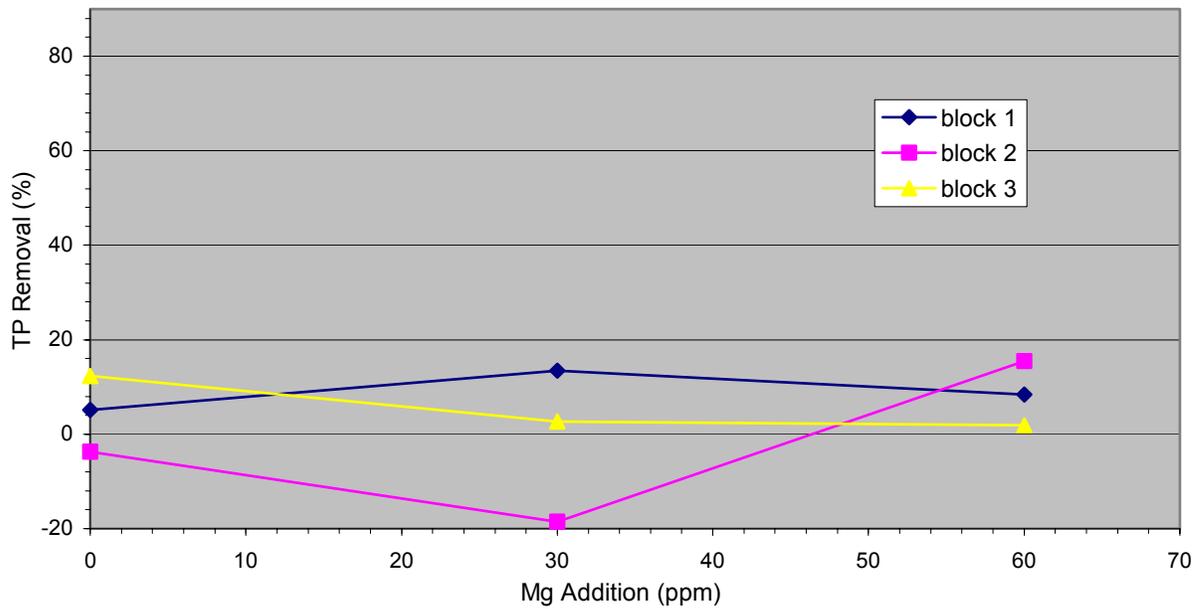


Figure 31: MVRs: TP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 41.2 L/h Flow

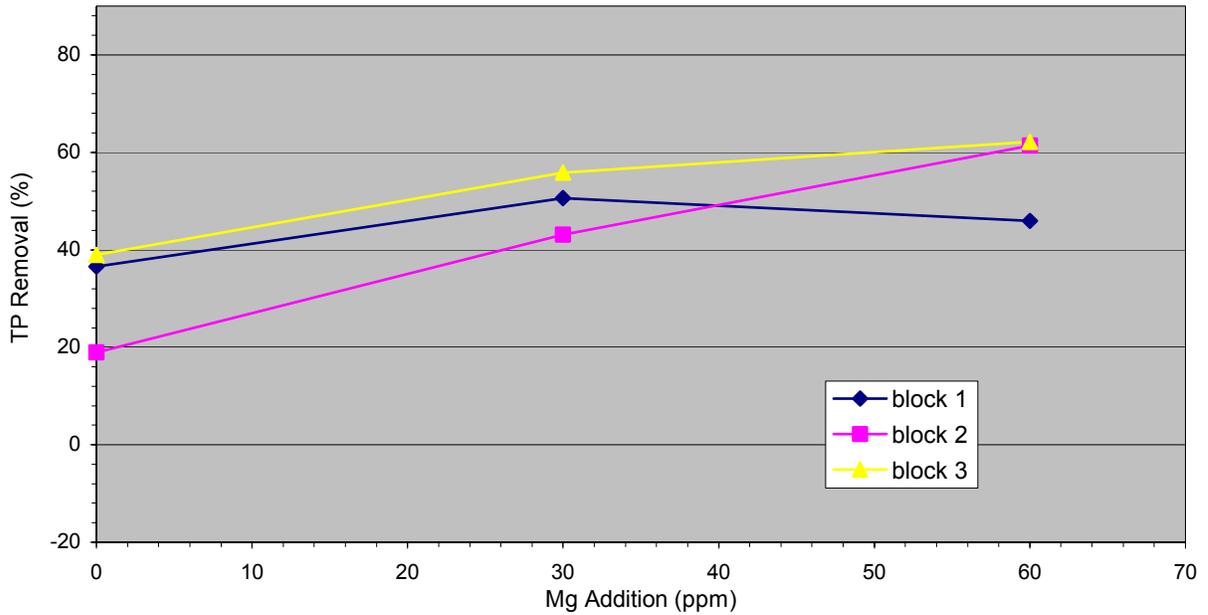


Figure 32: MVRs: TP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as TAN) Ammonia and 41.2 L/h Flow

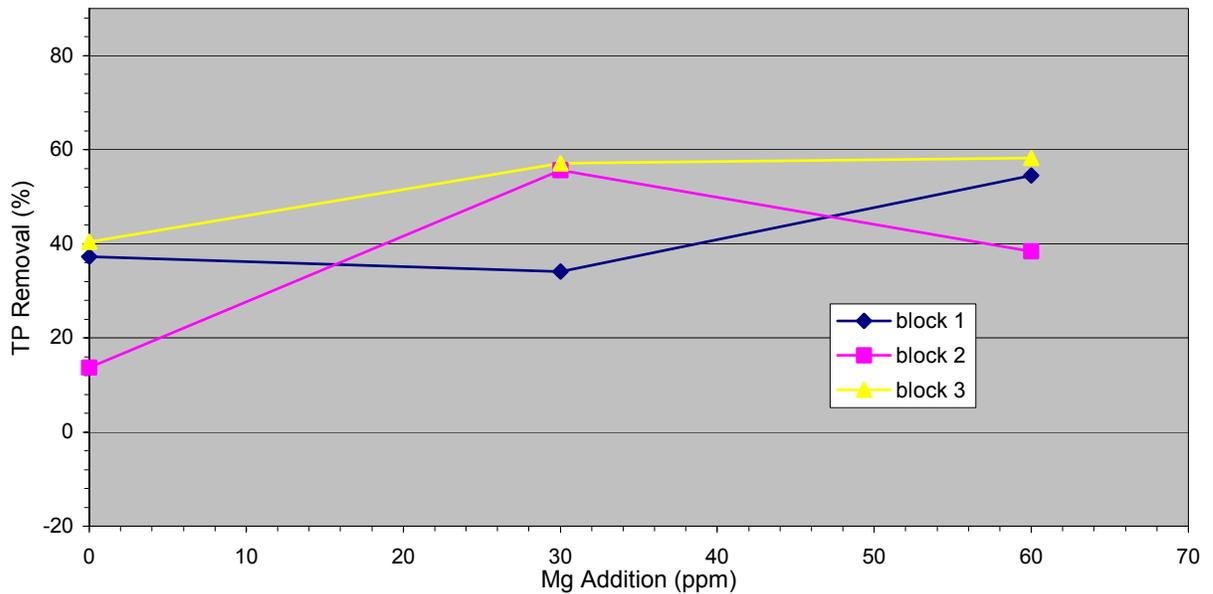


Figure 33: MVRs: TP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as TAN) Ammonia and 41.2 L/h Flow

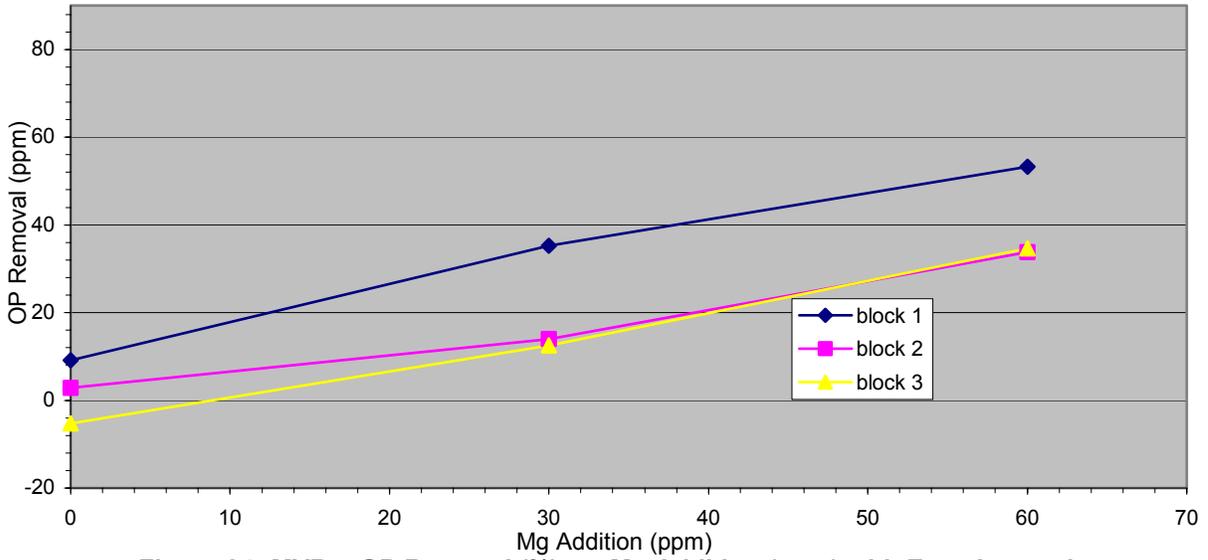


Figure 34: MVRs: OP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 56.8 L/h Flow

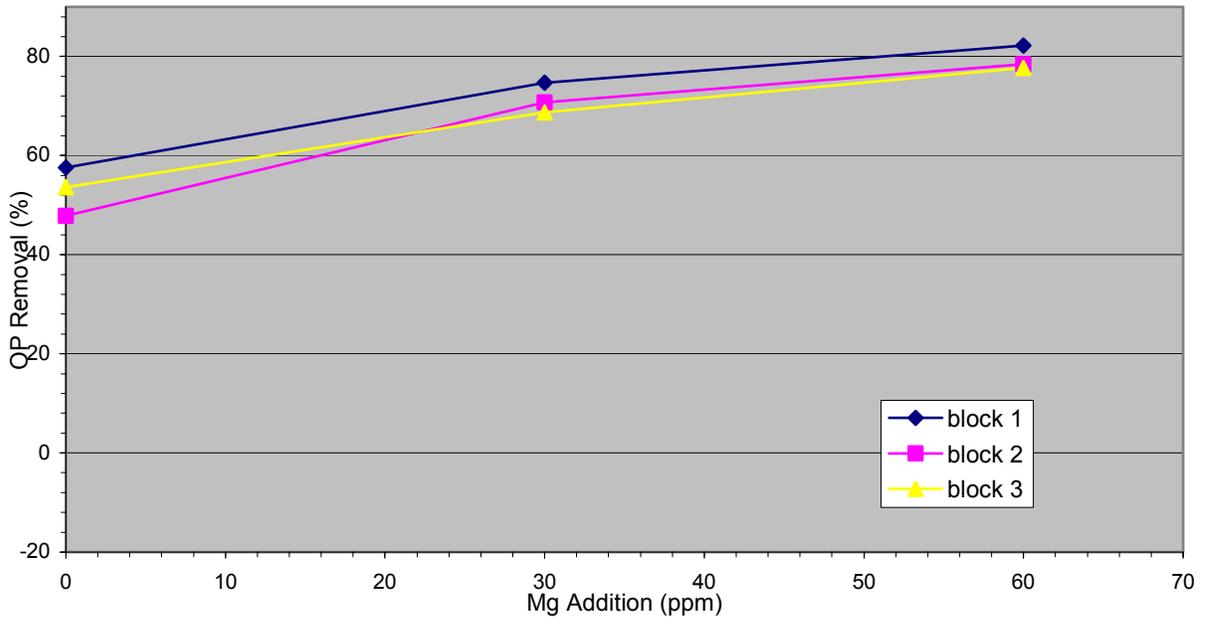


Figure 35: MVRs: OP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as TAN) Ammonia and 56.8 L/h Flow

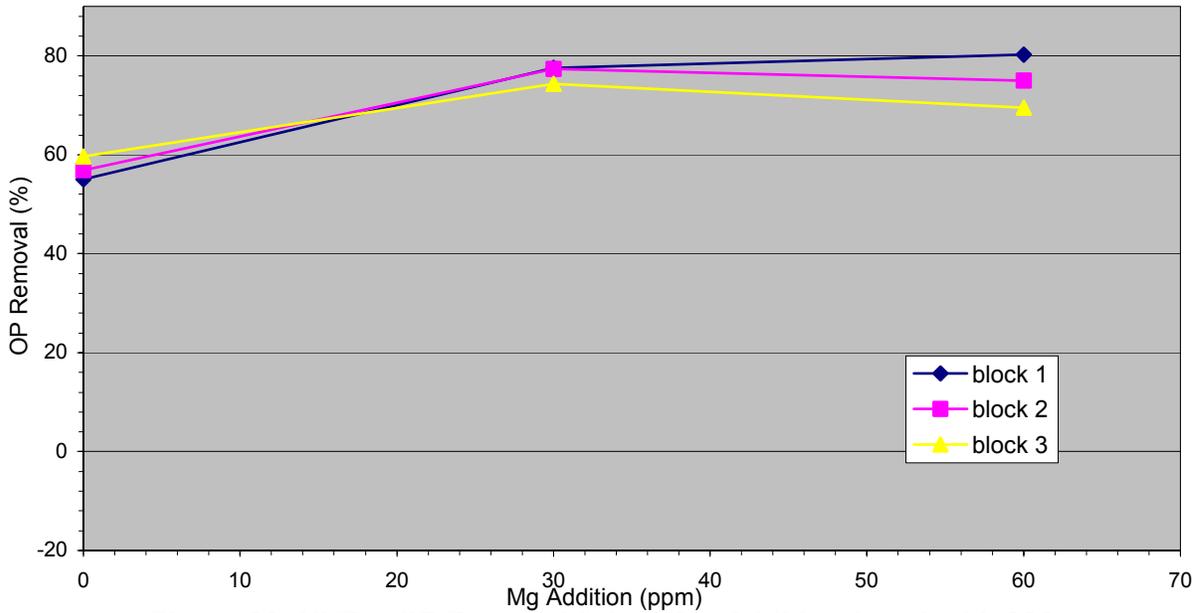


Figure 36: MVRs: OP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as TAN) Ammonia and 56.8 L/h Flow

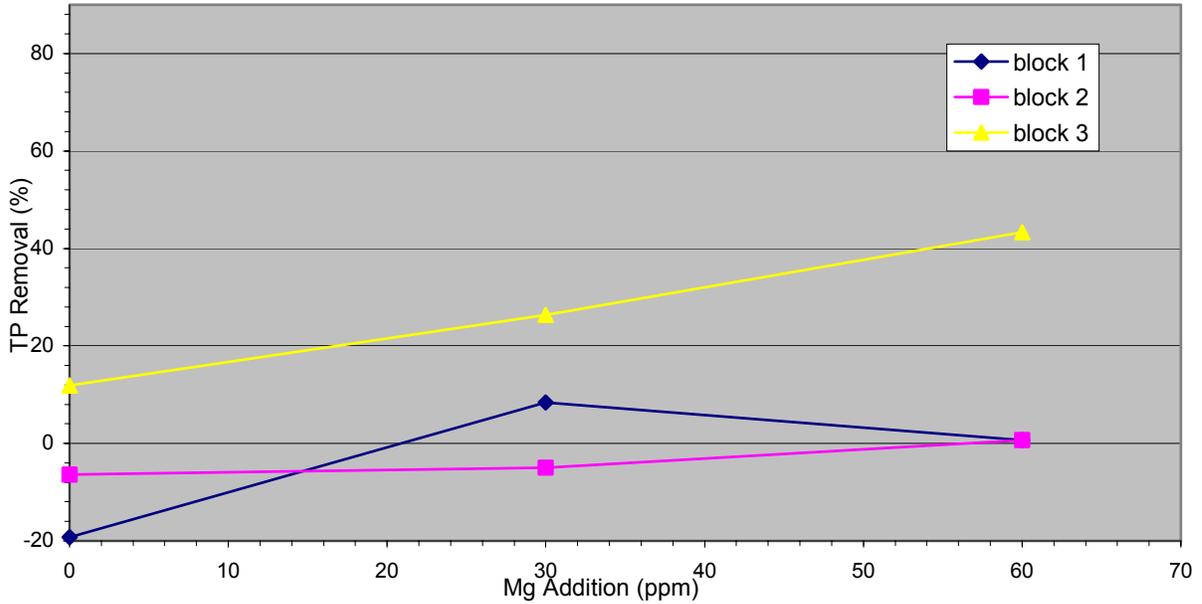


Figure 37: MVRs: TP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 56.8 L/h Flow

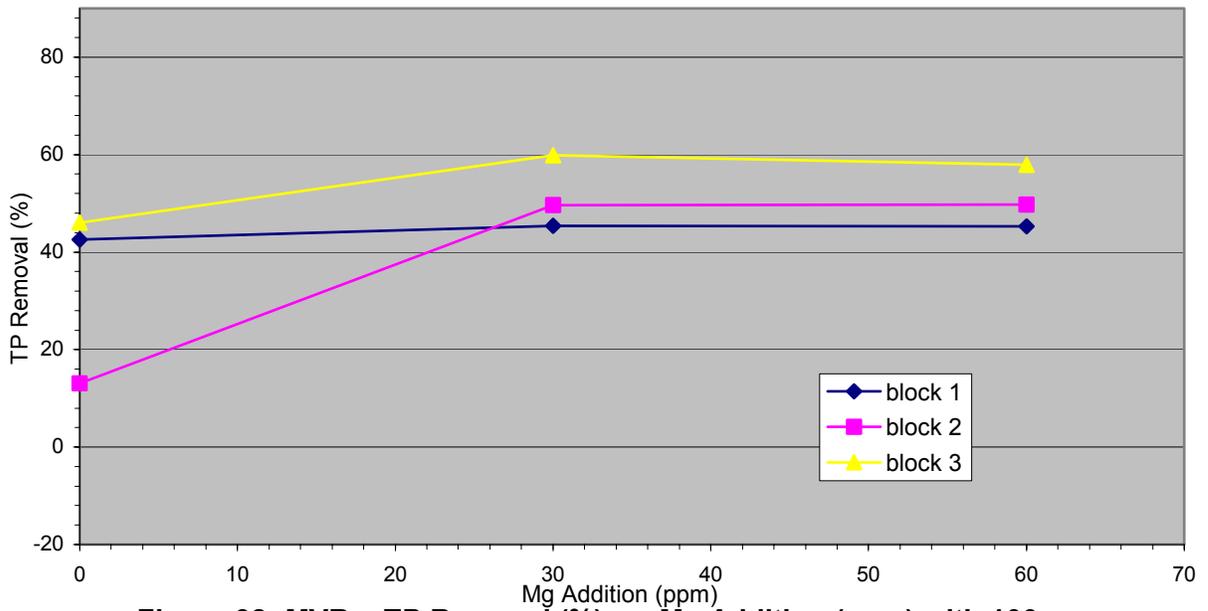


Figure 38: MVRs: TP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as N) Ammonia and 56.8 L/h Flow

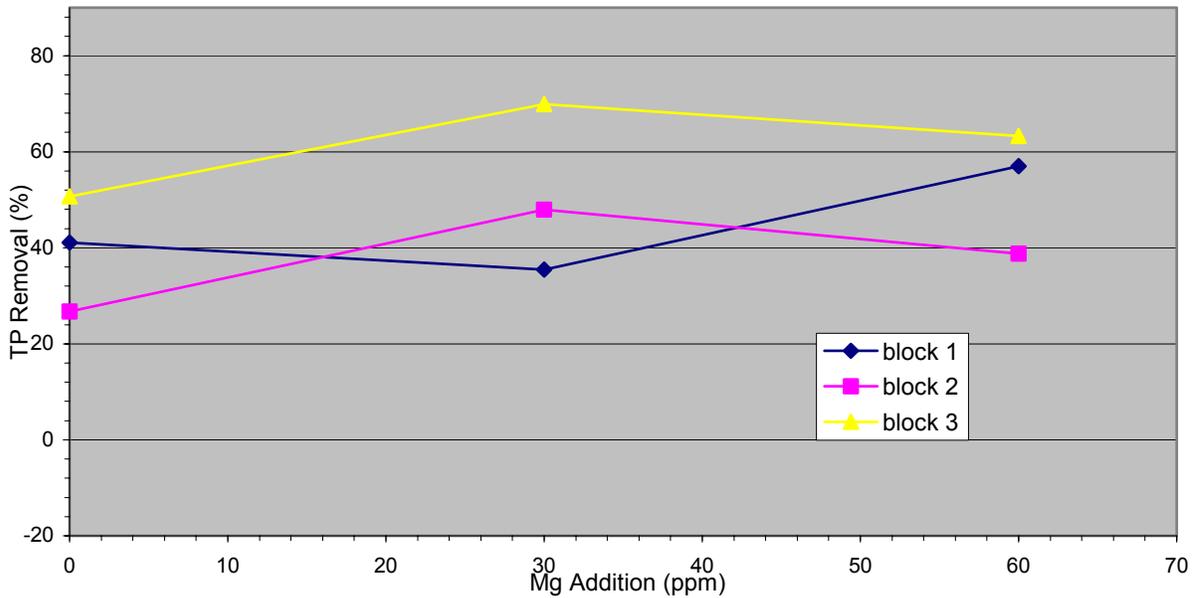


Figure 39: MVRs: TP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as N) Ammonia and 56.8 L/h Flow

phosphorus reduction was generally achieved in the second and third figure of each group of three (i.e., the higher two ammonia addition levels) than in the first (i.e., zero ammonia addition), meaning that phosphorus reduction was higher at the higher levels of ammonia addition. Again, the trend looks stronger in moving from the lowest level to the medium level than in moving from the medium to highest level.

Some other observations can be made. First, the range in phosphorus reduction is near that documented in the runs in the first stage, except that less phosphorus reduction is achieved when no ammonia is added. Second, TP reduction was less than OP reduction. Third, in some cases reductions in one block exceeded those for the other blocks at all three Mg levels (block 1 in Figures 28, 29, 34, and 35; block 3 in Figures 33, 37, 38, and 39). Finally, six instances of negative reduction were recorded, all occurring with zero ammonia addition and Mg at one of its two lower levels.

Statistical analyses treating OP reduction as the dependent variable and ammonia addition, Mg addition, and flow rate as fixed independent variables were conducted. An analysis of variance including the effect of blocks (treated as a random, rather than fixed, independent variable because it is useless in predicting phosphorus reduction) and of the fixed independent variables, including their three simple effects and all fourteen quadratic effects and interactions, was first performed to identify significant effects. Significant effects are here defined as those with associated p-values of 0.02 or less. The significant effects identified were (1) block; (2) simple effect of ammonia; (3) simple effect of Mg; (4) ammonia and Mg interaction; (5) ammonia quadratic effect; and (6) Mg quadratic effect. (Quadratic effect of a variable is weakening or strengthening of its effect with increasing level of the variable. For example, a negative quadratic effect of an independent variable means that increasing it when it is already at a high level yields less increase in the dependent variable than it yields when the independent variable is lower.) A summary of this analysis of variance is presented in Table 11.

**Table 11: Analysis of Variance for OP Reduction,
Including All Effects of All Independent Variables**
(Significant effects, with p-value 0.02 or less, indicated in bold type)

Source	Sum of Squares	Degrees of Freedom	Mean Square	F value	p-value
Block	754.4	1	754.4	23.9	< 0.0001
Block x block	173.8	1	173.8	5.5	0.0250
Ammonia	20721.6	1	20721.6	655.7	< 0.0001
Flow	0.05	1	0.05	0.0	0.9693
Magnesium	5983.0	1	5983.0	189.3	< 0.0001
Ammonia x magnesium	321.2	1	321.2	10.16	0.0031
Flow x magnesium	26.2	1	26.2	0.83	0.3691
Ammonia x flow	1.7	1	1.7	0.05	0.8162
Ammonia x ammonia	6040.5	1	6040.5	191.16	< 0.0001
Magnesium x magnesium	222.2	1	222.2	7.03	0.0121
Ammonia x ammonia x magnesium	8.4	1	8.4	0.27	0.6094
Ammonia x ammonia x flow	0.4	1	0.4	0.01	0.9094
Ammonia x magnesium x magnesium	174.8	1	174.8	5.53	0.0246
Ammonia x flow x magnesium	54.0	1	54.0	1.71	0.1999
Flow x magnesium x magnesium	4.6	1	4.6	0.15	0.7050
Ammonia x ammonia x magnesium x magnesium	16.1	1	16.1	0.51	0.4800
Ammonia x ammonia x flow x magnesium	26.4	1	26.4	0.84	0.3671
Ammonia x flow x magnesium x magnesium	7.0	1	7.0	0.22	0.6416
Ammonia x ammonia x flow x magnesium x magnesium	11.9	1	11.9	0.38	0.5427
Error	1074.4	34	31.6	--	--

Then, using only the five identified effects of the fixed independent variables, a new analysis of variance (Table 12) and a regression (Table 13) were performed. The new analysis of variance again showed all five of the effects to be significant, with p-values less than 0.02.

**Table 12: Analysis of Variance for OP Reduction,
Including Only the Significant Effects of the Fixed Independent Variables**

Source	Sum of Squares	Degrees of Freedom	Mean Square	F value	p-value
Ammonia	20721.6	1	20721.6	426.1	< 0.0001
Magnesium	5983.0	1	5983.0	123.0	< 0.0001
Ammonia x magnesium	321.2	1	321.2	6.6	0.0133
Ammonia x ammonia	6040.5	1	6040.5	124.2	< 0.0001
Magnesium x magnesium	222.2	1	222.2	4.6	0.0377
Error	2334.3	48	48.6	--	--

**Table 13: Regression of OP Reduction
Against Significant Effects of the Fixed Independent Variables**

Parameter	Estimate	Standard Error of Estimate
Intercept	3.4268	2.5552
Ammonia	0.7252	0.0443
Magnesium	0.8385	0.1475
Ammonia x magnesium	-0.0012	0.0005
Ammonia x ammonia	-0.0022	0.0002
Magnesium x magnesium	-0.0048	0.0022

Using the estimated coefficients from the regression yields the following equation for predicting OP removal:

$$\begin{aligned}
 OPR = & 3.43 + 0.725(AM) + 0.83(MG) - 0.00122(AM \times MG) \\
 & - 0.00224(AM \times AM) - 0.0048(MG \times MG)
 \end{aligned}
 \tag{43}$$

where *OPR* = percent reduction in orthophosphate phosphorus;

AM = ppm (as N) ammonia addition; and

MG = ppm Mg addition.

The same statistical analyses were repeated, this time treating TP reduction as the dependent variable. The analysis of variance that includes the effect of block and of the fixed independent variables and their interactions and quadratic effects is summarized in Table 14. The effects revealed

**Table 14: Analysis of Variance for TP Reduction,
Including All Effects of All Independent Variables**
(Significant effects, with p-value 0.02 or less, indicated in bold type)

Source	Sum of Squares	Degrees of Freedom	Mean Square	F value	p-value
Block	1298.4	1	1298.4	12.5	0.0012
Block x block	1650.5	1	1650.5	15.9	0.0003
Ammonia	14480.1	1	14480.1	139.2	< 0.0001
Flow	69.4	1	69.4	0.7	0.4198
Magnesium	2448.6	1	2448.6	23.5	< 0.0001
Ammonia x magnesium	37.2	1	37.2	0.4	0.5535
Flow x magnesium	0.3	1	0.3	0.0	0.9547
Ammonia x flow	9.0	1	9.0	0.1	0.7704
Ammonia x ammonia	4907.3	1	4907.3	47.2	< 0.0001
Magnesium x magnesium	221.6	1	221.6	2.1	0.1536
Ammonia x ammonia x magnesium	91.4	1	91.4	0.9	0.3553
Ammonia x ammonia x flow	49.6	1	49.6	0.5	0.4945
Ammonia x magnesium x magnesium	126.7	1	126.7	1.2	0.2775
Ammonia x flow x magnesium	178.8	1	178.8	1.7	0.1987
Flow x magnesium x magnesium	46.0	1	46.0	0.4	0.5104
Ammonia x ammonia x magnesium x magnesium	62.2	1	62.2	0.6	0.4447
Ammonia x ammonia x flow x magnesium	76.7	1	76.7	0.7	0.3966
Ammonia x flow x magnesium x magnesium	125.6	1	125.6	1.2	0.2795
Ammonia x ammonia x flow x magnesium x magnesium	0.5	1	0.5	0.0	0.9477
Error	3536.4	34	104.0	--	--

as significant by the analysis were fewer than in OP analysis, namely (1) block and quadratic block; (2) simple effect of ammonia; (3) simple effect of Mg; and (4) quadratic effect of ammonia.

The analysis of variance and the linear regression, using only the fixed effects indicated as significant, are summarized in Tables 15 and 16. Again, a p-value of less than 0.02 is associated with each of the effects.

**Table 15: Analysis of Variance for TP Reduction,
Including Only the Significant Effects of the Fixed Independent Variables**

Source	Sum of Squares	Degrees of Freedom	Mean Square	F value	p-value
Ammonia	14480.1	1	14480.1	95.5	< 0.0001
Magnesium	2448.6	1	2448.6	16.2	0.0002
Ammonia x ammonia	4907.3	1	4907.3	32.4	< 0.0001
Error	7580.2	50	151.6	--	--

**Table 16: Regression of TP Reduction
Against Significant Effects of the Fixed Independent Variables**

Parameter	Estimate	Standard Error of Estimate
Intercept	-2.8027	3.5543
Ammonia	0.6050	0.0740
Magnesium	0.2749	0.0684
Ammonia x ammonia	-0.0020	0.0004

Using the regression coefficients, the following predictive equation for reduction in TP can be formed:

$$TPR = -2.81 + 0.605(AM) + 0.275(MG) - 0.00202(AM \times AM) \quad (44)$$

where “TPR” signifies total phosphorus reduction, and “AM” and “MG” have the same meaning as in the regression equation for OP reduction.

Discussion of Results in MVRs

The range in phosphorus reduction in the MVRs mostly adheres to expectations built upon observations in the FCRs. The greatest difference is that lower reductions were seen in some cases than in any FCRs. However, these lower reductions in the MVRs occurred at times of zero ammonia addition, a condition never tested in the FCRs. The six cases of observed negative reduction were less expected. Possible causes of negative reduction include (1) random error in phosphorus sampling and/or analysis in cases where reduction was actually zero or slightly positive; (2) slight reduction in pH due to acidity in the Mg solution, leading to dissolution of some phosphorus-containing bed material and liberation into the liquid stream; and (3) phosphorus reduction in the cone insufficient to

compensate for the phosphorus input resulting from the phosphorus impurities in the material used to produce the Mg solution.

The simple effects of both Mg and ammonia to increase reduction in both OP and TP, which were revealed in the statistical analyses, are consistent with the overall upward trends observed in the plots. These simple effects also comport with the overall hypothesis for the mechanism of phosphorus reduction: that supersaturation with respect to struvite solubility leads to precipitation of phosphorus onto the bed material.

The negative quadratic effects seen in the statistical analysis also can be seen in the plots. The higher gains in reduction noted earlier in the plots in going from the lowest to the middle level of ammonia or Mg than in going from the middle level to the highest level evidence these effects.

The quadratic effects may result from the fact that the middle levels of Mg and ammonia addition are sufficient to push the rate high enough to achieve phosphorus removal near equilibrium and, because removal by struvite precipitation cannot surpass equilibrium, the additions of even more Mg and ammonia are less effective at precipitating additional phosphorus. Another possibility is that the middle levels of addition push the equilibrium phosphorus concentration quite low, and further additions of ammonia or Mg lead to less dramatic decreases. Yet a third possibility is that the highest levels of addition supersaturate the liquid sufficiently to produce spontaneous nucleation, which would limit phosphorus reduction because of small particles carrying over in the treated liquid.

All three explanations, however, seem as if they should apply as well to the quadratic effect of Mg on TP, which the analyses indicated was not significant, as it does to the three quadratic effects that were indicated to be significant. Perhaps Mg addition throughout the Mg range speeds some unrecognized mechanism of non-orthophosphate phosphorus removal. Perhaps there really is a negative quadratic effect, but not strong enough to generate a high-confidence signal in this experiment. Note that the p-value associated with this effect was the lowest among the fourteen effects with p-values greater than 0.05.

The negative interaction effect of Mg and ammonia indicated as significant for OP reduction suggests that further supersaturation from moderate levels achieves less additional OP reduction than supersaturation to the moderate levels, even when the additive used to achieve the higher level is not the same as the additive used to achieve the moderate level (i.e., ammonia to moderately supersaturate and Mg to further supersaturate). The same three explanations offered for the negative quadratic effects may thus also be considered for the negative interaction effect. Again, the effect is not indicated as significant for TP reduction, and again an unrecognized mechanism for non-orthophosphate phosphorus removal may be considered. However, the hypothesis that random error obscures the negative quadratic effect is less plausible in this case because the p-value is quite low.

The indication by the analyses that flow rate has no significant effect on phosphorus removal is consistent with the observation that the appearance of the plots of data at 41.2 L/h appear very similar to those at 56.8 L/h. The lack of effect suggests that the surface area for reaction provided in the bed is more than sufficient, at the lower flow rate, for the reaction to proceed to near equilibrium by the time the liquid exits the bed. The phosphorus concentration at the lower rate, then, would drop very quickly to near equilibrium in the lower half of the bed then remain nearly constant through the upper portion. As the flow rate increased, the point at which the concentration reached to near-equilibrium would rise higher in the bed, and eventually, at some higher flow rate, the liquid would exit the bed without having had sufficient time to approach equilibrium. At this point, flow rate would become a significant factor in phosphorus removal. As discussed under the results from the first stage, which was conducted at a flow rate half-way between the low and high flow rates here, the phosphorus concentration profile was observed to drop very fast to a near-constant level somewhere in the mid-portion of the bed. That observation provides evidence in favor of this explanation for the lack of flow rate effect.

The low p-values for block and quadratic block effects indicate differences among the blocks in TP and OP reductions. This result is consistent with the earlier-noted observation that phosphorus

reductions were at times higher for blocks 1 and 3. The differences among blocks cannot be attributed to any known variation; rather, it can be considered random experimental error resulting from differences in the raw liquid, sample handling, and/or sample testing among the blocks, each of which was conducted on a different day with a different batch of raw liquid. That there is variation among the blocks is not a surprise. The design of the experiment incorporated blocks in this fashion specifically to remove these day-to-day variations from the rest of the variability, thus revealing the effects of ammonia, Mg, and flow more sharply.

Equations (43) and (44) were used to predict the optimum levels of Mg and ammonia addition for, respectively, OP reduction and TP reduction. For OP reduction, the predicted optimum of 83.7% reduction is at 143 ppm ammonia addition and 68 ppm Mg addition. These are the values of AM and MG that yield zero values for the partial differentials of equation (43) with respect to AM and MG . Applying the same method to equation (44) produces a value of 150 ppm ammonia addition to optimize TPR reduction, but there is no value of MG that will yield a zero value for the partial differential of equation (44) with respect to MG . This result, which is expected because the equation is linear in MG rather than quadratic, means that equation (44) predicts no optimum amount of Mg addition; i.e., the trend of increasing TP removal with increases in Mg addition holds true at all levels of Mg addition. For ammonia addition at the optimum level and Mg addition at its highest tested value, equation (44) predicts TP removal of 59.0%, the highest predicted level in the tested addition ranges.

Care must be exercised in interpreting these optima because they apply specifically to the lagoon liquid tested. As a first approximation, 140 to 150 ppm ammonia may be predicted as the optimum level for TP and OP reduction in effluent from a typical North Carolina lagoon. However, differences in TAN and/or phosphorus concentrations, pH levels, or other variables could shift the optima. Moreover, Mg addition predicted optima must be viewed with caution because they lie outside the tested range, subject to effects not observed in the MVRs. Reduction in OP may not

actually reach a maximum at 68 ppm Mg addition and then begin decreasing beyond that point.

Other trends may prevail outside the tested range, resulting in a higher optimum. Likewise, trends not evidenced in the tested range may result in a non-infinite optimum in Mg addition for TP reduction.

The ammonia addition levels may be viewed as pH rises by one considering use of an alkali or alkaline substance other than ammonia. The peaks in TP and OP reduction are predicted at around 150 ppm ammonia addition. In the MVRs, 200 ppm addition was observed to produce pH rises of 1.2 to 1.3 points above the pH of the raw lagoon liquid, and 100 ppm resulted in rises of about 0.8 to 0.9 pH points. If one accepts an assumption that the effect of pH rise on phosphorus reduction will be the same regardless of what substance induces the pH rise, then phosphorus reductions near the maximum predicted in the MVR range would be expected when adding enough of the alternative alkali or alkaline substance to increase pH by an amount roughly mid-way between the two observed rises, or about 1.0 to 1.1 pH points.